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CXXXII.—*The Formation and Hydrolysis of Esters of Ketonic Acids.*

By JOHN JOSEPH SUDBOROUGH.

IN a previous paper (Trans., 1908, **93**, 210) the values for the esterification constants of the normal fatty acids at 15° have been given when methyl alcohol and the hydrogen chloride catalytic method are used. The values obtained indicate that formic acid is the most readily esterified under these conditions; then follow acetic and propionic acids, and the acids from butyric to stearic have practically the same constant, namely, about 50.

As a continuation of this work the esterification constants of some of the commoner ketonic acids (α, β, and γ) have been determined in order to ascertain the effect of the replacement of a methylene, CH_2, group by carbonyl.

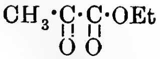
Kailan (*Monatsh.*, 1907, **28**, 1187) has determined the constant for phenylglyoxylic acid (benzoylformic), using an impure sample, and states that it is esterified less readily than the analogously constituted phenylacetic acid:

$C_6H_5\cdot CO\cdot CO_2H$	$C_6H_5\cdot CH_2\cdot CO_2H.$
Phenylglyoxylic acid.	Phenylacetic acid.

This would indicate that a carbonyl group in the α-position with respect to the carboxyl group produces a retarding effect on esterification when the catalytic method is employed.

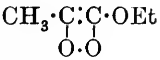
Stewart's experiments on the relative activities of the carbonyl groups in ketonic compounds (Trans., 1905, **87**, 185; Proc., 1905, **21**, 78) are of interest in connexion with this work on the esterification of ketonic acids and on the hydrolysis of the esters of such acids.

According to Stewart, in the carbonyl groups of α-ketonic esters and of α-diketones a redistribution of affinity occurs owing to intramolecular vibrations, and as a result of this a rearrangement of valencies takes place, which can be expressed by such formulæ as:



$CH_3\cdot\underset{\underset{O}{\|}}{C}\cdot\underset{\underset{O}{\|}}{C}\cdot OEt$

and



$CH_3\cdot\underset{\underset{O}{|}}{C}:\underset{\underset{O}{|}}{C}\cdot OEt$.

In the analogous case of *o*-benzoquinone, two isomeric forms have been isolated by Willstätter and Müller (*Ber.*, 1908, **41**, 2580).

The rearrangement of affinity or of valencies in the case of α- and β-ketonic esters produces an increase in the chemical activity of the carbonyl group, and, similarly, an increase in the reactivity of the carbonyl group of the carboxylic radicle might be expected.

ll our results show that as regards esterification the presence of a ırbonyl group in the α- or β-position with respect to the carboxylic roup does not increase the activity of the latter group. In all the ıses investigated it has the opposite effect when the catalytic ıethod of esterification is used.

The fact that in an acid like pyruvic, $CH_3{\cdot}CO{\cdot}CO_2H$, the carboxyl roup increases the activity of the carbonyl group, whereas the ırbonyl group appears to have no similar effect on the carboxyl roup, is capable of a simple explanation.

In the carboxyl group itself it is highly probable that the ydrogen atom is not attached permanently to the same oxygen om, so that a change represented by the scheme:

$$-\mathrm{C}\!\begin{array}{l}\nearrow\!\mathrm{O}\\ \searrow\!\mathrm{OH}\end{array} \rightleftarrows -\mathrm{C}\!\begin{array}{l}\nearrow\!\mathrm{OH}\\ \searrow\!\mathrm{O}\end{array},$$

continuously taking place. Such a rearrangement would produce highly reactive carbonyl group and hydrogen atom, and would ccount for the fact that the hydrogen atoms of carboxylic groups re more reactive than those of alcoholic or phenolic hydroxylic roups.

In the case of an α-ketonic acid any rearrangement of valencies etween the carbonyl and carboxylic groups will produce an ıcreased reactivity of the carbonyl group, but not necessarily of the ırboxyl group, as any rearrangement of valencies in this, due to ıe presence of the α-carbonyl group, will occur only at the expense f the change:

$$-\mathrm{C}\!\begin{array}{l}\nearrow\!\mathrm{O}\\ \searrow\!\mathrm{OH}\end{array} \leftrightarrows -\mathrm{C}\!\begin{array}{l}\nearrow\!\mathrm{OH}\\ \searrow\!\mathrm{O}\end{array}$$

lready referred to.

As a further extension of our work we have attempted to esterify ıe ketonic acids pyruvic, lævulic, and benzoylacetic at the ordinary emperature in the absence of a catalytic agent. We have also udied the hydrolysis of the esters of these acids by means of ater, dilute hydrochloric acid, and dilute barium hydroxide lution. The results obtained are discussed in the sections dealing ith the respective experiments.

EXPERIMENTAL.

I.—*Esterification of Ketonic Acids by the Hydrogen Chloride Catalytic Method.*

A. *With Methyl Alcohol.*

Propionic Acid.—For purposes of comparison the value of $E^{15^\circ}_{\mathrm{MeOH}}$ or propionic acid, previously determined (Trans., 1908, **93**, 212), given, namely, 91·9.

Pyruvic Acid, $CH_3\cdot CO\cdot CO_2H$.—Some difficulty was met with in titrating mixtures of the acid and ester in methyl alcohol. When standard barium hydroxide was used with phenolphthalein as indicator, it was found that the ester was hydrolysed extremely readily by the strong alkali, and the pink colour was far too transitory for accurate titrations to be made; in fact, anything approaching a permanent coloration was obtained only after the complete hydrolysis of the ester originally present. Better results were obtained when the feebler alkali ammonium hydroxide was used in conjunction with litmus as indicator. Kailan (*loc. cit.*) experienced a similar difficulty in titrating mixtures of mandelic acid and its ester, and used ammonium hydroxide with rosolic acid as indicator.

A. Concentration of the hydrogen chloride after mixing $= 0{\cdot}03241N$. 15 c.c. of the alcoholic solution required 20·25 c.c. of $0{\cdot}09442N\text{-}NH_4OH$.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0·5	12·1	0·447
0·75	9·0	0·470
1·0	7·2	0·449
1·25	5·7	0·440

B. Concentration of the hydrogen chloride after mixing $= 0{\cdot}03241N$. 15 c.c. of the alcoholic solution required 15·75 c.c. of $0{\cdot}09442N\text{-}NH_4OH$.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0·33	10·80	0·497
0·5	9·05	0·481
0·67	7·80	0·455
1·0	5·60	0·449

C. Concentration of the hydrogen chloride after mixing $= 0{\cdot}02310N$. 15 c.c. of the alcoholic solution required 19·7 c.c. of $0{\cdot}09442N\text{-}NH_4OH$.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0·2	16·65	0·366
0·5	12·85	0·371
0·7	11·05	0·359
1·0	8·85	0·348
1·2	7·70	0·340

Corrected for N-HCl: $A = 13{\cdot}93$. $B = 14{\cdot}51$. $C = 15{\cdot}44$.

$$E^{15^\circ}_{MeOH} = 14{\cdot}62 \times 2{\cdot}303 = 33{\cdot}7.$$

Benzoylacetic Acid, $C_6H_5\cdot CO\cdot CH_2\cdot CO_2H$.—The acid used was Schuchardt's acid, which was boiled for some little time with light petroleum (b. p. 40—60°), filtered, and washed with the hot solvent. When heated it melted and decomposed at 97—98°, whereas Perkin (Trans., 1884, **45**, 176) gives the point of decomposition as 103—104° when heated quickly. The acid was not quite pure, as was shown by titration with standard barium hydroxide solution, using phenolphthalein as indicator:

0·2 gram required 31·75 c.c. of 0·03664N-barium hydroxide.
Theory requires 33·3 c.c.

Difficulties were experienced in titrating mixtures of this acid and its ester (ethyl). When barium hydroxide is used, an appreciable amount of the alkali is taken up by the ester; but when ammonium hydroxide is used the amount of alkali which neutralises the ester is not so large.

A solution of 0·906 gram of pure ethyl benzoylacetate in 100 c.c. of absolute alcohol was prepared; 30 c.c. of this solution was mixed with distilled water, and required 1·0 c.c. of 0·0396N-ammonium hydroxide solution before a neutral coloration was obtained with litmus as indicator; 20 c.c. required 0·75 c.c. and 13 c.c. required 0·45 c.c. It is thus obvious that in titrating mixtures of acid and ester against standard ammonium hydroxide, the readings obtained will not give correct values for the concentration of the acid present, as a part of the alkali is used up in reacting with the ester.

In determining the esterification constant the values obtained for $a-x$ will not be the correct values, and they will differ from the correct values the greater the proportion of ester present. In making a determination of $E^{15^\circ}_{\mathrm{MeOH}}$ in the usual manner, we found that the value of K diminished from 0·107 to 0·0905. In order to obtain fairly correct values for $a-x$, and hence for K, we made several experiments by mixing solutions of benzoylacetic acid and hydrogen chloride in methyl alcohol, and titrating after a short interval of time so that the amount of ester present should be small.

0·8 Gram of benzoylacetic acid was made up to 100 c.c. with methyl alcohol; 15 c.c. of this solution required 15·34 c.c. of 0·04577N-ammonium hydroxide.

Equal volumes (15 c.c.) of this solution and of a 0·0564N-solution of hydrogen chloride were mixed and titrated after a few minutes. The results were:

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0·0417	14·9	0·303
0·0833	14·6	0·257
0·0833	14·5	0·293
0·1667	13·8	0·276

Mean corrected for N-hydrogen chloride = 10·0. $E^{15^\circ}_{\mathrm{MeOH}} = 23·0$.

Laevulic Acid, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$.—The acid used was Kahlbaum's pure acid, which distilled at 149—150°/19 mm., and solidified to a hard, crystalline cake melting at 33°.

A. Concentration of the hydrogen chloride after mixing = 0·02278N. 15 c.c. of the alcoholic solution required 32·95 c.c. of 0·03664N-barium hydroxide.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0·5	24·25	0·266
0·75	20·65	0·270
1·0	17·65	0·271
1·25	15·05	0·272
1·5	13·20	0·265
1·75	11·25	0·267

B. Concentration of the hydrogen chloride after mixing = 0·03140N. 15 c.c. of the alcoholic solution required 27·85 c.c. of 0·03664N-barium hydroxide.

(in hours).	$a-x$.	$1/t \log a/a-x$.
0·25	22·80	0·348
0·50	18·75	0·334
0·75	15·20	0·351
0·85	14·15	0·346
1·0	12·60	0·344
1·25	10·55	0·338
1·4	9·25	0·342

Mean corrected for N-HCl: $A = 11·8$. $B = 11·0$.

$E^{15^\circ}_{\mathrm{MeOH}} - 11·4 \times 2·303 = 26·2$.

Some little difficulty was experienced in titrating mixtures of the acid and ester in methyl alcohol. A pink coloration was produced, but this disappeared in the course of a few minutes, and a fair amount of barium hydroxide solution was required to restore the colour. It was also found that when water was added to the mixture before the barium hydroxide solution was run in, the amount of alkali required was greater than before. At first it was thought that these phenomena were due to the readiness with which the ester was hydrolysed by water or dilute hydrochloric acid. Subsequent experiments made with the pure ester (compare pp. 1236 and 1231) proved that it is not readily hydrolysed, and can be kept in contact with water for days and with dilute hydrochloric acid for several hours without appreciable hydrolysis. The values for K obtained by titrating the alcoholic solutions with barium hydroxide and taking the reading when the pink coloration was first produced after stirring, varied considerably. The only method of obtaining good results is to add water to the alcoholic mixture, and wait for some five to ten minutes before titrating with the standard barium hydroxide solution. In this way a sharp end-point is obtained, the pink coloration remains permanent for an hour or more, and the values for K agree remarkably well.

We can offer no explanation of the above phenomena unless they are to be attributed to the slow ionisation of the feeble acid, lævulic acid.

The esterification constant of lævulic acid has been determined by a method similar to that used in the case of pyruvic acid, namely, using standard ammonium hydroxide for titrating, and litmus as indicator. The end-point is not sharp, however, owing to the fact that lævulic acid is a very feeble acid, $K=0{\cdot}00255$ (Ostwald, *Zeitsch. physikal. Chem.*, 1889, **3**, 418), and fairly good results can only be obtained by working to a standard neutral tint. The numbers obtained were of much the same order of magnitude as when barium hydroxide and phenolphthalein were used.

β-Benzoylpropionic Acid, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$.—The acid was prepared from cinnamaldehydecyanohydrin by hydrolysis with dilute hydrochloric acid (Peine, *Ber.*, 1884, **17**, 2114), and after several crystallisations from water was obtained in needles melting at 117—118°.

The dissociation constant obtained by Hantzsch and Miolati (*Zeitsch. physikal. Chem.*, 1892, **10**, 23) was 0·00221.

Concentration of the hydrogen chloride after mixing = 0·0202*N*. 15 c.c. of the alcoholic solution required 25·58 c.c. of 0·02941*N*-barium hydroxide.

(in hours).	$a-x$.	$1/t \log a/a-x$.
0·5	19·2	0·249
0·6	18·2	0·246
0·7	17·25	0·244
0·8	16·3	0·245

B. Concentration of the hydrogen chloride after mixing = 0·0202*N*. 15 c.c. of the alcoholic solution required 25·76 c.c. of 0·02941*N*-barium hydroxide.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0·4	20·2	0·264
0·6	18·3	0·247
0·8	16·4	0·245
1·0	14·9	0·238

Mean corrected for *N*-HCl: $A = 12·2$. $B = 12·3$.

$$E^{15}_{MeOH} = 12·25 \times 2·303 = 28·2.$$

γ-Benzoylbutyric Acid, $C_6H_5·CO·[CH_2]_3·CO_2H$.—The acid was prepared by hydrolysing ethyl *αβ*-dibenzoylglutarate (Knoevenagel, *Annalen*, 1894, **281**, 33) with 10 per cent. aqueous potassium hydroxide solution (Kuhn, *Annalen*, 1898, **302**, 216), and after crystallisation from water was obtained in glistening plates melting at 128°.

A. Concentration of the hydrogen chloride after mixing = 0·02331*N*. 15 c.c. of the alcoholic solution required 25·73 c.c. of 0·02941*N*-barium hydroxide.

(in hours)	$a-x$.	$1/t \log a/a-x$.
0·3	17·32	0·573
0·4	15·42	0·556
0·55	13·12	0·532

B. Concentration of the hydrogen chloride after mixing = 0·01093*N*. 15 c.c. of the alcoholic solution required 25·73 c.c. of 0·02941*N*-barium hydroxide.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0·5	19·1	0·259
0·7	17·05	0·255
0·9	15·4	0·248
1·1	13·9	0·243

Mean corrected for *N*-HCl: $A = 23·8$. $B = 23·0$.

$$E^{15°}_{MeOH} = 23·4 \times 2·303 = 53·9.$$

The following table gives a comparison of the esterification constants of the ketonic acids with those for the corresponding acids containing a methylene group in place of carbonyl:

Ketonic Acid.	$E^{15°}_{MeOH}$.	Methylene Acid.	$E^{15°}_{MeOH}$.
Pyruvic, $CH_3·CO·CO_2H$	33·8	Propionic	91·9*
Benzoylacetic, $C_6H_5·CO·CH_2·CO_2H$	24·4	*β*-Phenylpropionic	47·3†
Lævulic, $CH_3·CO·CH_2·CH_2·CO_2H$	25·9	*n*-Valeric	53·5*
β-Benzoylpropionic, $C_6H_5·CO·[CH_2]_2·CO_2H$	28·2	*γ*-Phenylbutyric	56·3†
γ-Benzoylbutyric, $C_6H_5·CO·[CH_2]_3·CO_2H$	53·9	*δ*-Phenylvaleric	39·5†

* Sudborough and Gittins, Trans., 1908, **93**, 211.

† *Ibid.*, Trans., 1909, **95**, 319.

These results indicate that the carbonyl group in the *α*-, *β*-, or *γ*-position has a retarding effect on the rate of esterification as compared with a methylene group in the same position. The behaviour of *γ*-benzoylbutyric acid is somewhat anomalous, as it appears to be esterified more readily than *δ*-phenyl-*n*-valeric acid.

The retarding effect of the carbonyl group, although well marked, is not of the same magnitude as the effect of an ethylene linking (compare Trans., 1909, **95** 315), for example, crotonic acid has $E^{15°}_{MeOH}$ 1·28, whereas *n*-butyric acid has $E^{15°}_{MeOH}$ 50·0. In a ketonic acid, $O{:}CMe{\cdot}CO_2H$, a double linking is introduced between the α-carbon atom and oxygen, but this has not the same marked effect on esterification by the catalytic method as the introduction of a double linking between the α- and β-carbon atoms.

B. *With Ethyl Alcohol.*

We have determined the esterification constants of some of the ketonic acids at 15°, using an ethyl-alcoholic solution of hydrogen chloride, the chief object being to ascertain whether the ratio $E^{15°}_{MeOH} : E^{15°}_{EtOH}$ is practically a constant for different acids.

The alcohol used was Kahlbaum's 99·8 per cent., which had been distilled twice with small amounts of calcium, namely, 0·25 and 0·5 per cent. of the weight of alcohol.

Propionic Acid.

A. Concentration of the hydrogen chloride after mixing = 0·02473*N*. 15 c.c. of the alcoholic solution required 38·65 c.c. of 0·03664*N*-barium hydroxide.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0·5	33·75	0·118
1·0	29·65	0·115
1·5	25·95	0·115
2·0	22·95	0·113
3·0	17·85	0·112

B. Concentration of the hydrogen chloride after mixing = 0·02198*N*. 15 c.c. of the alcoholic solution required 29·4 c.c. of 0·03664*N*-barium hydroxide.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0·5	26·0	0·107
0·75	24·5	0·106
1·25	21·8	0·104
1·75	19·4	0·103
2·25	17·3	0·102

Mean corrected for N-HCl : $A=4{\cdot}65$. $B=4{\cdot}75$.

$E^{15°}_{EtOH}=10{\cdot}8$.

◆

Pyruvic Acid.

A. Concentration of the hydrogen chloride after mixing = 0·06973*N*. 15 c.c. of the alcoholic solution required 16·55 c.c. of 0·0936*N*-ammonium hydroxide.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0·38	14·75	0·132
1·5	10·05	0·144
2·0	8·65	0·141
2·5	7·45	0·139
3·0	6·45	0·136

B. Concentration of the hydrogen chlorride after mixing = 0·02243*N*. 15 c.c. of the alcoholic solution required 10·65 c.c. of 0·0936*N*-ammonium hydroxide.

t (in hours).	$a-x$.	$1/t \log a/a-x$
1·5	9·15	0·440
2·0	8·70	0·440
3·0	7·80	0·451
4·25	6·90	0·444

Mean corrected for N-HCl : $A=1{\cdot}98$. $B=1{\cdot}98$.

$E^{15°}_{EtOH}=4{\cdot}58$.

Laevulic Acid.

A. Concentration of the hydrogen chloride after mixing $=0·02552N$. 15 c.c. of the alcoholic solution required 31 c.c. of $0·03664N$-barium hydroxide.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
1·5	26·8	0·0422
2·5	24·55	0·0405
4·0	21·45	0·0400
5·0	19·65	0·0396

B. Concentration of the hydrogen chloride after mixing $=0·02552N$. 15 c.c. of the alcoholic solution required 30·5 c.c. of $0·03664N$-barium hydroxide.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0·5	29·1	0·0408
1·0	27·6	0·0434
1·75	25·75	0·0420
2·25	24·6	0·0415
2·75	23·7	0·0398
4·0	21·1	0·0400
7·75	15·3	0·0387

Mean corrected for N-HCl: $A=1·59$. $B=1·60$.

$E^{15°}_{EtOH}=3·67$.

These numbers gave the following values for the ratio $E^{15°}_{MeOH} : E^{15°}_{EtOH}$.

Propionic,	8·5 : 1.
Pyruvic,	7·5 : 1.
Lævulic,	7·1 : 1.

II.—*Esterification of Ketonic Acids by the Direct Method at* 15°.

Solutions of the respective acids in methyl alcohol were prepared. Each solution was carefully titrated, and the remainder divided into small portions (15 to 30 c.c.), which were placed in small stoppered bottles in a thermostat at 15°, and titrated after given intervals of time.

The following are the results obtained:

Propionic Acid.—Even after one hundred and ninety-two hours practically no esterification had occurred, as indicated by the following numbers:

t (in hours)	0	21	69	119	192
Titration in c.c. of barium hydroxide...	27·1	27·1	27·02	27·0	26·9

Pyruvic Acid.—

A. 1·6295 grams dissolved in methyl alcohol.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0	19·9	—
48	18·7	0·000565
96	17·9	0·000479
146	17·3	0·000416
194	16·7	0·000393
291	15·9	0·000335
416	14·9	0·000302

B. 1·093 grams were made up to 100 c.c. with methyl alcohol.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
0	26·55	—
51	24·5	0·000682
96	23·9	0·000476
169	21·7	0·000518
310	19·9	0·000403

Laevulic Acid.—After two hundred and fourteen hours practically no ester was formed, as indicated by the following numbers:

t (in hours)	0	46	70	96	168	214
C.c. of barium hydroxide ...	56·5	56·5	56·4	56·45	56·5	56·4

Similar results were obtained when ethyl alcohol was used.

Benzoylacetic Acid.—A solution of 3·0 grams of benzoylacetic acid in 200 c.c. of methyl alcohol was prepared; 15 c.c. of the freshly prepared solution required 13·15 c.c. of 0·0936*N*-ammonium hydroxide. After twenty-eight hours 15 c.c. of the same solution required less than 2 c.c. of the ammonium hydroxide solution for neutralisation, but the end-point was not at all well defined. The addition of 2 c.c. of the ammonium hydroxide solution produced a decided blue coloration, but within two seconds the red colour was restored. The addition of 4 c.c. of the alkali solution, however, produced a permanent blue coloration. These numbers appeared to indicate that the benzoylacetic acid was esterified with great rapidity by the direct method. The fact that the end-point was not sharp, and that on opening the bottles after they had remained for some time a slight pressure was observed, pointed to another possibility, namely, the decomposition of the benzoylacetic acid into acetophenone and carbon dioxide. We were able to prove that this decomposition does occur to a very appreciable extent.

0·4 Gram of the acid was dissolved in methyl alcohol, and placed in a bottle which was connected by a rubber stopper and delivery tube to a second bottle containing barium hydroxide solution. The barium hydroxide was protected from atmospheric carbon dioxide by means of a soda-lime tube. After some eighteen hours a copious precipitate of barium carbonate was deposited, showing that appreciable amounts of carbon dioxide had been evolved from the benzoylacetic acid solution.

Of the acids examined the only one which is esterified at all readily by the direct method at 15° is pyruvic. An examination of the dissociation constants of the acids:

Propionic, $K=0·00134$ (Ostwald)
Lævulic, $K=0·00255$ („)
Pyruvic, $K=0·56$ (Hantzsch and Miolati),

at once indicates that pyruvic acid is a much stronger acid than the other acids examined, and thus confirms the conclusion drawn some years ago by Sudborough and Lloyd (Trans., 1899, **75**, 481) that the strength of an acid is of primary importance in the esterification by the direct (autocatalytic) method, whereas when the catalytic (hydrogen chloride) method is used this factor appears to be negligible.

The values obtained for pyruvic acid show that the reaction cannot be regarded as a unimolecular reaction. Our numbers are not sufficiently numerous or accurate for us to discuss the question whether the reaction is bimolecular or not (compare Wegscheider, *Ber.*, 1896, **29**, 1896; Kailan, *Monatsh.*, 1907, **28**, 1203).

III.—*Hydrolysis of the Esters by Means of Water.*

Methyl propionate, ethyl propionate, ethyl pyruvate, and ethyl lævulate were examined as they were sufficiently soluble in water.

Of these the only ester which was hydrolysed appreciably by water was ethyl pyruvate. Methyl propionate, ethyl propionate, and ethyl lævulate solutions were practically neutral, even after some three weeks; thus 10 c.c. of a solution containing 1·29 grams of ethyl lævulate per 100 c.c. gave an alkaline reaction to litmus on the addition of one drop of standard ammonium hydroxide solution, and a similar result was obtained after the solution had been kept at 15° for three weeks.

The following results were obtained with ethyl pyruvate:

A. 1·0875 Grams of ester were made up to 100 c.c. with freshly boiled distilled water. The solution was placed in a thermostat at 15°, and 10 c.c. were removed at intervals and titrated with 0·09442*N*-ammonium hydroxide. $a=19·85$.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
67	18·75	0·000370
115	17·85	0·000401
187	16·45	0·000437
335	13·15	0·000534
452	10·05	0·000654

B. 2·333 Grams of the same ester were made up to 250 c.c. with distilled water $a=17·05$.

t (in hours).	$a-x$.	$1/t \log a/a-x$.
68·5	16·05	0·000382
164·5	14·75	0·000381
283·5	12·55	0·000469
367 5	11·10	0·000507
499·0	8·40	0·000616
552·0	7·65	0·000630
597·0	6·95	0·000652
674 0	5·45	0·000734
717·0	5·05	0 000737
840·0	3·80	0·000776
1058·0	2·15	0·000850

The results obtained show that the dissociation constant of the acid from which the ester is derived is an important factor in the hydrolysis of an ester by means of water. Esters derived from strong acids are hydrolysed at an appreciable rate by water at the ordinary temperature, whereas those derived from feeble acids are not.

The numbers given by ethyl pyruvate prove that in dilute solution the reaction cannot be regarded as a simple unimolecular reaction, as the values for K increase rapidly with t when the equation for a unimolecular reaction is employed for calculating K. These results are in harmony with the view that the hydrolysis is due to hydrions, and the number of these increases as the hydrolysis proceeds.

IV.—*Hydrolysis of Esters by means of Dilute Hydrochloric Acid.*

The general method adopted was to prepare standard solutions of the ester and of hydrogen chloride in distilled water, to mix equal volumes of these at 15°, and then to remove 10 or 20 c.c. of the mixture by means of a calibrated pipette after given intervals of time, and to titrate with standard barium hydroxide solution using phenolphthalein as indicator, or in the case of ethyl pyruvate titrating with standard ammonium hydroxide and litmus.

The following table gives the results obtained:

Ester.	Series.	Conc. of HCl.	No. of titrations.	Max. time, hours.	$1/t \log a/a-x$. Min.	$1/t \log a/a-x$. Max.	K calculated for N-HCl.
Methyl propionate...	*a*	0·05N	10	212	0·00334	0·00340	0·0676
	b	0·05N	11	211	0·00330	0·00348	
Ethyl propionate ...	*a*	0·05N	12	235	0·00350	0·00362	0·0714
	b	0·05N	11	214	0·00351	0·00362	
Ethyl pyruvate	*a*	0·04645N	6	238	0·00378	0·00409	0·0865
	b	0·04645N	5	140	0·00410	0·00416	
Methyl lævulate......	*a*	0·05N	12	760	0·00064	0·00067	0·0130
	b	0·05N	12	819	0·00064	0·00066	
Ethyl lævulate	*a*	0·04645N	8	576	0·00060	0·00068	0·0126
	b	0·04645N	7	598	0·00060	0·00066	

The values for the hydrolysis constants of the various esters using normal hydrochloric acid are given in the last column. The results indicate that methyl and ethyl esters derived from the same acid are hydrolysed at much the same rate, but that in each pair of compounds examined the ethyl ester is decomposed a little more quickly than the methyl ester:

K Ethyl propionate : K methyl propionate = 1·051
K Ethyl lævulate : K methyl lævulate = 1·034

These ratios agree with values obtained by Hemptinne (*Zeitsch. physikal. Chem.*, 1894, **13**, 562) for the ratios of the hydrolysis constants of the ethyl and methyl esters of acetic, propionic, and butyric acids at 25°, namely, 1·031. The results also show that the introduction of a carbonyl group into the α-position with respect to the carbethoxy-group has only a slight effect on the rate of hydrolysis of an ester by means of dilute mineral acid, for example:

K Ethyl pyruvate : K methyl propionate = 1·2

The constants for methyl and ethyl lævulate are considerably less than those for the other esters, just as the constant for ethyl *n*-valerate is less than that for ethyl propionate:

K Ethyl propionate : K ethyl valerate = 5·06 at 25°
K Ethyl propionate : K ethyl lævulate = 5·25 at 15°

Hydrolysis by means of Barium Hydroxide Solution.

The impossibility of titrating mixtures of pyruvic acid with one of its esters when standard barium hydroxide is used, indicates the readiness with which the esters of this acid are hydrolysed by alkalis as compared with the esters of propionic and lævulic acids. This confirms the conclusion previously drawn by Sudborough and Lloyd (Trans., 1899, **75**, 482), namely, that the strength of the acid from which the ester is derived is an important factor in saponification by alkalis.

I have to thank Mr. J. M. Gittins for assistance in determining some of the esterification constants.

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CXXXIII.—*Some Hydroxy-ketonic Dyes.*

By JATINDRA MOHAN DUTTA and EDWIN ROY WATSON.

IN a previous paper (*J. Soc. Chem. Ind.*, 1911, **30**, 196) in an investigation into the relation between chemical constitution and fastness to light and other agencies of the simplest hydroxy-ketone dyes, namely, the polyhydroxybenzophenones, we noted that two xanthone derivatives, 1:2-dihydroxyxanthone and 1:2:7-trihydroxyxanthone, did not seem to possess any superiority as dyes over the polyhydroxybenzophenones from which they had been formed by condensation. This suggested the question whether the γ-pyrone ring, in any of the xanthones or flavones containing it, contributed anything to the value of these dyes, and whether the polyhydroxyphenyl styryl ketones and polyhydroxybenzylacetophenones might not possess dyeing properties equally as good as the corresponding flavones. Butein, a dyestuff obtained from the flowers of *Butea frondosa* (A. G. Perkin and Hummel, Trans., 1904, **85**, 1459), has been assigned the constitution 2:4-dihydroxyphenyl 3:4-dihydroxystyryl ketone, $C_6H_3(OH)_2\cdot CO\cdot CH{:}CH\cdot C_6H_3(OH)_2$, and possesses very interesting dyeing properties, giving, in fact, deeper shades than any of the flavones or flavanoles.

By the condensation of cinnamic acid and β-phenylpropionic acid respectively with pyrogallol we have obtained 2:3:4-*trihydroxyphenyl styryl ketone*, $C_6H_2(OH)_3\cdot CO\cdot CH{:}CH\cdot C_6H_5$, and 2:3:4-*tri-*

hydroxybenzylacetophenone, $C_6H_2(OH)_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$. These compounds have dyeing properties very similar to those of the polyhydroxybenzophenones already examined. By the condensation of *o*-hydroxycinnamic acid with pyrogallol and resorcinol respectively we have obtained compounds which are probably *pyrogallolhydroxycinnamein*:

$$\left.\begin{array}{l} C_6H_2(OH)_3{\cdot}C(OH)(CH{:}CH{\cdot}C_6H_4{\cdot}OH){\cdot}C_6H_2(OH)_2 \\ C_6H_2(OH)_3{\cdot}C(OH)(CH{:}CH{\cdot}C_6H_4{\cdot}OH){\cdot}C_6H_2(OH)_2 \end{array}\right>O = C_{42}H_{34}O_{15}$$

and *resorcinol-hydroxycinnamein*:

$$\left.\begin{array}{l} C_6H_3(OH)_2{\cdot}C(OH)(CH{:}CH{\cdot}C_6H_4{\cdot}OH){\cdot}C_6H_3(OH) \\ C_6H_3(OH)_2{\cdot}C(OH)(CH{:}CH{\cdot}C_6H_4{\cdot}OH){\cdot}C_6H_3(OH) \end{array}\right>O = C_{42}H_{34}O_{11}.$$

They dye much deeper shades than were expected from the theoretically simplest condensation products, namely, 2:3:4-*trihydroxyphenyl 2-hydroxystyryl ketone* and 2:4-*dihydroxyphenyl 2-hydroxystyryl ketone*. The compound from hydroxycinnamic acid and resorcinol is especially interesting as giving very full and beautiful crimson and purple shades. Its properties have considerable resemblance to those of resorcinol-benzein (*Ber.*, 1894, **27**, 1997). 2:4-*Dihydroxyphenyl 2-hydroxystyryl ketone*,

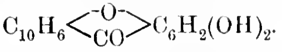
$$C_6H_3(OH)_2{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OH,$$

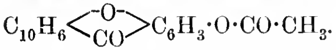
has been synthesised by condensing together resacetophenone and salicylaldehyde in concentrated alcoholic potassium hydroxide solution according to a method recently described by Goschke and Tambor (*Ber.*, 1911, **44**, 3503), and has quite different properties.

In attempting to prepare the acetyl derivatives of the compounds above described by boiling with acetic anhydride and a trace of pyridine, 2:3:4-trihydroxyphenyl styryl ketone yielded cinnamic anhydride; no crystalline products were isolated from this treatment of 2:3:4-trihydroxybenzylacetophenone, or of the substances obtained by the condensation of *o*-hydroxycinnamic acid with pyrogallol and resorcinol.

None of the polyhydroxybenzophenones gives shades deeper than yellow or orange-yellow on alum mordant, and this, no doubt, is the reason why they find little application. Reasoning from analogy to the monoazo-series of dyes, it would seem possible that the colour might be deepened by replacing one or both of the benzene nuclei by naphthalene nuclei. One compound of this type, a tetrahydroxyphenyl naphthyl ketone, has been described (*Ber.*, 1890, **23**, 188) as being produced from the condensation of α-naphthol and gallic acid. By repeating the condensation we did not succeed in obtaining this substance. By the condensation of β-naphtholcarboxylic acid with pyrogallol and resorcinol respectively we have obtained 2:3:4-trihydroxyphenyl 2-hydroxy(3)-naphthyl ketone, $C_6H_2(OH)_3{\cdot}CO{\cdot}C_{10}H_6{\cdot}OH$, and 2:4-*dihydroxyphenyl*

2-hydroxy(3)-*naphthyl ketone*, $C_6H_3(OH)_2\cdot CO\cdot C_{10}H_6\cdot OH$. The compounds do not, however, dye shades appreciably deeper than the polyhydroxybenzophenones.

In attempting to prepare the acetyl derivatives of these hydroxy-derivatives of phenyl naphthyl ketone by boiling with acetic anhydride and a trace of pyridine, or better with a trace of zinc chloride, instead of their corresponding acetyl derivatives, the acetyl derivatives of the corresponding xanthones were obtained; thus 2:3:4-trihydroxyphenyl 2-hydroxy(3)-naphthyl ketone gave a *monoacetyl* derivative of the corresponding dihydroxynaphthaxanthone,  $C_{10}H_6{<}\begin{smallmatrix}-O-\\ CO\end{smallmatrix}{>}C_6H_2(OH)_2$, but its diacetyl derivative could not be prepared. 2:4-Dihydroxyphenyl 2-hydroxy(3)-naphthyl ketone gave *acetoxynaphthaxanthone*,



$$C_{10}H_6{<}\begin{smallmatrix}-O-\\ CO\end{smallmatrix}{>}C_6H_3\cdot O\cdot CO\cdot CH_3.$$

The hydroxynaphthaxanthones themselves have been prepared; 3:4-*dihydroxynaphthaxanthone* was obtained by heating trihydroxyphenyl hydroxynaphthyl ketone in sealed tubes according to the Graebe and Eichengrün method (*Ber.*, 1891, **24**, 969); and also by the hydrolysis of the monoacetyl derivative of dihydroxynaphthaxanthone according to Perkin's method (Trans., 1905, **87**, 107). The other xanthone, namely, *monohydroxynaphthaxanthone*, was prepared by the hydrolysis of acetoxynaphthaxanthone. They are both light yellow, crystalline substances. Their dyeing properties have not yet been tested.

EXPERIMENTAL.

2:3:4-*Trihydroxyphenyl Styryl Ketone*, $C_6H_2(OH)_3\cdot CO\cdot CH{:}CH\cdot C_6H_5$.

Four grams of cinnamic acid and 4·5 grams of pyrogallol were mixed together and heated in an oil-bath. When the mixture melted, 8 grams of powdered anhydrous zinc chloride were gradually added, and the heating was continued with constant stirring for forty to forty-five minutes at 115—120°. The mass was then extracted with boiling water, boiled for half-an-hour with 350 c.c. of water and a little animal charcoal, and filtered hot. The filtrate on cooling deposited the new compound in chocolate-coloured, plate-like crystals. It was recrystallised from boiled water, and dried in the steam-oven. The yield was about 50 per cent. of the cinnamic acid used. The substance melts at 125—126°, dissolves in alkalis with a bright yellow colour, and dyes mordanted wool in the following shades: light yellow on alum, greenish-yellow on chrome, grey on iron, and light pink on tin:

0·2182 gave 0·5646 CO_2 and 0·100 H_2O. C=70·59; H=5·09.
$C_{15}H_{12}O_4$ requires C=70·31; H=4·70 per cent.

2:3:4-*Trihydroxybenzylacetophenone*,
$C_6H_2(OH)_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$.

Three grams of β-phenylpropionic acid and 2·8 grams of pyrogallol were mixed together and heated in an oil-bath. When the mixture melted, 8 grams of powdered anhydrous zinc chloride were gradually added, and the heating was continued with constant stirring for about two hours at 115—120°. The fusion was then extracted with 50 c.c. of absolute alcohol, and the alcoholic solution boiled for about half an hour with a little animal charcoal and then filtered hot. To it was added 200 c.c. of water, and the new compound separated in prismatic crystals, which were recrystallised from dilute alcohol. The yield was about 60 per cent. of the β-phenylpropionic used. The substance has a light pink colour. It crystallises with a molecule of water, and melts at 86—87°. It dissolves in alkalis with a yellow colour, and dyes mordanted wool in the following shades: yellow on alum, yellowish-brown on chrome, dark grey on iron, and very light yellow on tin:

0·1890 gave 0·4606 CO_2 and 0·0981 H_2O. C=65·46; H=5·77.
$C_{15}H_{14}O_4,H_2O$ requires C=65·22; H=5·79 per cent.

Pyrogallol-hydroxycinnamein.

Four grams of *o*-hydroxycinnamic acid and 4 grams of pyrogallol were mixed together and heated in an oil-bath. When the mixture melted, 8 grams of powdered anhydrous zinc chloride were gradually added, and the heating was continued with constant stirring at 135—140° for one and a-quarter hours. The mass was then extracted with alcohol, the alcoholic solution filtered hot, and hot water added until turbidity was produced. On cooling a precipitate was obtained which was not obviously crystalline. It was collected, dried, and purified by precipitating from acetic acid solution. It melts at 170°. The substance precipitated from alcohol and washed with very dilute hydrochloric acid has the same melting point. Its alkaline solution is deep brown, and it dyes wool in the following shades on the different mordants: maroon on alum, dark brown on chrome, dark grey on iron, and cerise on tin. After being dried at 100°:

0·1267 gave 0·2969 CO_2 and 0·0547 H_2O. C=63·91; H=4·80.
$2C_{42}H_{34}O_{15},H_2O$ requires C=64·03; H=4·44 per cent.

Resorcinol-hydroxycinnamein.

Three grams of *o*-hydroxycinnamic acid and 2 grams of resorcinol were mixed together and heated in an oil-bath. When the mixture melted, 6 grams of powdered anhydrous zinc chloride were added gradually, and the heating continued for nearly an hour at 115° with constant stirring. The mass was then extracted with alcohol, the alcoholic solution boiled with a little animal charcoal for a few minutes, and filtered hot. Hot water was added to it until turbidity appeared. After some time this solution deposited a deep scarlet precipitate, which was reprecipitated from alcohol. It melts at 124—126°, is readily soluble in alcohol, and insoluble in benzene. Its alkaline solution is of an intense red colour, and on dilution shows beautiful, green fluorescence. It dyes mordanted wool in the following shades: purplish-red on alum, crimson on chrome, deep purple on iron, and red on tin:

0·1043 gave 0·2455 CO_2 and 0·0493 H_2O. C = 64·07; H = 5·24.
$C_{42}H_{34}O_{11},4H_2O$ requires C = 64·11; H = 5·34 per cent.

2:4-*Dihydroxyphenyl 2-Hydroxystyryl Ketone*, $C_6H_3(OH)_2{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OH$.

This compound was prepared by heating resacetophenone and salicylaldehyde in alcoholic solution with concentrated potassium hydroxide solution. It crystallises from dilute alcohol in golden-yellow, needle-shaped crystals, and melts at 188°. It is readily soluble in alcohol, acetone, or ether, but insoluble in benzene or water. Its alkaline solution is red:

0·1341 gave 0·3468 CO_2 and 0·0582 H_2O. C = 70·53; H = 4·82.
$C_{15}H_{12}O_4$ requires C = 70·31; H = 4·69 per cent.

It dyes wool in the following shades: bright yellow on alum, orange on chrome, lemon-yellow on tin, yellowish-brown on iron.

2:3:4-*Trihydroxyphenyl 2-Hydroxynaphthyl Ketone*, $C_6H_2(OH)_3{\cdot}CO{\cdot}C_{10}H_6{\cdot}OH$.

β-Naphtholcarboxylic acid (m. p. 216°) and pyrogallol in molecular proportions were melted together, powdered anhydrous zinc chloride (twice the weight of the mixture) added, and the heating continued at 130—140° for three hours. The mass was extracted with alcohol, and the alcoholic solution, after decolorisation with animal charcoal and dilution with hot water, deposited on cooling the compound in stout, green, needle-shaped crystals. It was recrystallised from dilute alcohol. The yield was about 50 per cent. of the β-naphtholcarboxylic acid taken. The substance melts at

204—208° (Noelting and Meyer, *Ber.*, 1897, **30**, 2594, give 287—289°), dissolves in alkalis with a deep maroon colour, and dyes mordanted wool in the following shades: orange on alum, yellowish-brown on chrome, dark brown on iron, full yellow on tin. (Found, C = 68·61; H = 4·25. Calc., C = 68·91; H = 4·05 per cent.)

2:4-*Dihydroxyphenyl* 2-*Hydroxynaphthyl Ketone*, $C_6H_3(OH)_2\cdot CO\cdot C_{10}H_6\cdot OH$.

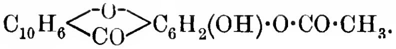
Prepared by condensing β-naphtholcarboxylic acid and resorcinol with anhydrous zinc chloride under exactly the same conditions as observed in the preceding preparation (compare Noelting and Meyer, *loc. cit.*). The yield was about the same as in that preparation. The new compound was recrystallised from dilute alcohol, and obtained in brown, plate-shaped crystals. It melts at 204—206°, dissolves in alkalis with a yellow colour, and dyes wool in the following shades, which are, however, only weak: yellow on alum, brown on chrome, brown on iron, yellow on tin:

0·1615 gave 0·4182 CO_2 and 0·0657 H_2O. C = 70·62; H = 4·52.
$2C_{17}H_{12}O_4,H_2O$ requires C = 70·59; H = 4·50 per cent.

Attempts to Acetylate 2:3:4-*Trihydroxyphenyl Styryl Ketone.*

This substance was boiled with acetic anhydride and a trace of pyridine. A white, crystalline compound was isolated from the reaction mixture, which proved to be cinnamic anhydride (m. p. 132°. Found, C = 77·70; H = 5·03. Calc., C = 77·70; H = 5·04 per cent.).

Monoacetyl Derivative of Dihydroxynaphthaxanthone,

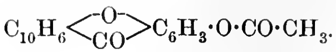


$$C_{10}H_6\Big\langle\begin{matrix}-O-\\CO\end{matrix}\Big\rangle C_6H_2(OH)\cdot O\cdot CO\cdot CH_3.$$

One gram of 2:3:4-trihydroxyphenyl 2-hydroxynaphthyl ketone was gently boiled with about 8 c.c. of acetic anhydride and 2 or 3 drops of pyridine for an hour. The solution was concentrated to half its bulk, and cooled. On adding absolute alcohol and scratching the sides of the containing tube, a white, crystalline substance was deposited. This was redissolved in a little acetic anhydride, boiled gently for fifteen minutes, and reprecipitated by absolute alcohol. It melts sharply at 200°:

0·1263 gave 0·3250 CO_2 and 0·0432 H_2O. C = 71·78; H = 3·80.
$C_{19}H_{12}O_5$ requires C = 71·37; H = 3·75 per cent.

Acetoxynaphthaxanthone,

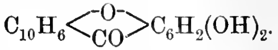


$C_{10}H_6{<}\substack{\text{-O-}\\ \text{CO}}{>}C_6H_3\cdot O\cdot CO\cdot CH_3.$

Prepared by acetylating 2:4-dihydroxyphenyl 2-hydroxynaphthyl ketone under the same conditions as in the preceding preparations. It was obtained in cream-coloured, needle-shaped crystals melting at 217°:

0·1280 gave 0·3529 CO_2 and 0·0444 H_2O. C=75·20; H=3·86.
$C_{19}H_{12}O_4$ requires C=75·00; H=3·95 per cent.

3:4-*Dihydroxynaphthaxanthone,*



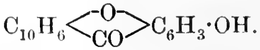
$C_{10}H_6{<}\substack{\text{-O-}\\ \text{CO}}{>}C_6H_2(OH)_2.$

One gram of trihydroxyphenyl hydroxynaphthyl ketone was heated in a sealed tube with 20 c.c. water for nine hours at 200—220°. On cooling, the condensation product separated in plates, which were collected and recrystallised from dilute alcohol, being obtained in small, plate-like crystals melting at 280—285°. A sample of it was dried at 120°, and then analysed:

0·1387 gave 0·3741 CO_2 and 0·0423 H_2O. C=73·56; H=3·39.
$C_{17}H_{10}O_4$ requires C=73·40; H=3·40 per cent.

This substance was also prepared by the hydrolysis of the mono-acetyl derivative of dihydroxynaphthaxanthone by Perkin's method (Trans., 1905, **87**, 107). 0·3 Gram of the acetyl compound was boiled with 5 c.c. of glacial acetic acid and 8 drops of concentrated sulphuric acid for five minutes. The mixture was then poured into about 100 c.c. hot water, which at once precipitated the dihydroxynaphthaxanthone. On cooling, this was collected and recrystallised from dilute alcohol.

Hydroxynaphthaxanthone,



$C_{10}H_6{<}\substack{\text{-O-}\\ \text{CO}}{>}C_6H_3\cdot OH.$

Prepared from acetoxynaphthaxanthone under the same conditions as in the preceding preparation. It separated from dilute alcohol in fine, lemon-yellow, needle-shaped crystals. The alcoholic solution exhibits a beautiful, blue fluorescence. It shows signs of melting at 280°, but does not melt even at 285°. A sample dried at 120° was analysed:

0 1262 gave 0·3629 CO_2 and 0·0404 H_2O. C=78·40; H=3·56.
$C_{17}H_{10}O_3$ requires C=77·86; H=3·81 per cent.

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CXXXIV.—*The Spectroscopic Investigation of the Carbinol-Ammonium Base Isomerism. Benziminazole and* iso*Quinoline Derivatives.*

By CHARLES KENNETH TINKLER.

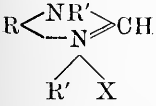
HARTLEY'S method of obtaining evidence in support of a particular formula for a tautomeric substance, from the agreement of its ultra-violet absorption spectra with those of one of its derivatives of known constitution, has been employed in several cases in connexion with the carbinol–ammonium base isomerism. Reference is made to several publications in this connexion in a paper by the author on the constitution of berberine (Trans., 1911, **99**, 1341).

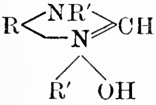
The present paper has to deal with the application of the method in the case of derivatives of benziminazole and of *iso*quinoline.

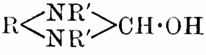
(a) *Benziminazole Derivatives.*

The action of alkalis on iminazolium salts has been very fully studied by Niementowsky and by O. Fischer and his co-workers. A summary of the work done in this connexion is given in a recent paper by Meldola and Kuntzen (Trans., 1911, **97**, 1290).

It is supposed that by the action of an alkali on the quaternary iminazolium salt (I) the free base (II) at first produced is converted into a carbinol (III):


(I.)


(II.)


$$R\left<\begin{matrix}NR'\\NR'\end{matrix}\right>CH\cdot OH$$
(III.)


$$R\left<\begin{matrix}-NR'-\\NHR'\end{matrix}\right>CHO$$
(IV.)

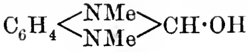
In no case apparently in connexion with these iminazole derivatives has it been suggested that an open-chain aldehydeamine (IV) is produced, although in other cases it has appeared usual to adopt this constitution for these pseudo-bases from purely chemical considerations.

The substances chosen for the investigation of this isomerism amongst iminazole compounds were dimethylbenziminazolium iodide (V) and its simple derivatives:


$$C_6H_4\left<\begin{matrix}NMe-\\NMeI\end{matrix}\right>CH$$
(V.)

The iodide is prepared by the action of methyl alcohol and methyl iodide on benziminazole, which results from the condensation of *o*-phenylenediamine and chloroform (O. Fischer, *Ber.*, 1901,

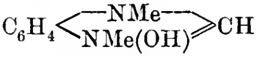
34, 930). On treatment with sodium hydroxide the quaternary iodide gives rise to a substance to which O. Fischer has assigned the carbinol formula of dimethylbenziminazolol (VI), the substance



$$C_6H_4 < \substack{NMe\\NMe} > CH\cdot OH$$

(VI.)

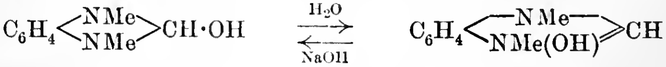
being produced by the migration of the hydroxyl group of dimethylbenziminazolium hydroxide (VII):



$$C_6H_4 < \substack{NMe\\NMe(OH)} > CH$$

(VII.)

The ultra-violet absorption spectra of a solution of dimethylbenziminazolium iodide in water and of the base obtained by treating this solution with silver oxide are identical. The latter solution has an alkaline reaction, and evidently contains the free azolium hydroxide. Freshly-made aqueous or alcoholic solutions of the carbinol give, however, spectra which are identical with those of the carbinol in alcoholic chloroform and alcoholic ether, but are quite distinct from those of the iodide and free azolium hydroxide. After being kept for some time the solutions in water and alcohol give spectra which are identical with those of the azolium hydroxide and iodide. The change, however, requires only a few hours in the case of the aqueous solution, but several weeks in the case of the alcoholic solution. This agreement of spectra of the solutions of the carbinol with those of the quaternary salt can only be explained by assuming that under the influence of the solvents the carbinol has been reconverted into the free azolium hydroxide:



$$C_6H_4 < \substack{NMe\\NMe} > CH\cdot OH \quad \underset{NaOH}{\overset{H_2O}{\rightleftarrows}} \quad C_6H_4 < \substack{NMe\\NMe(OH)} > CH$$

Confirmation of this view is obtained from the fact that the aqueous solution of the carbinol, which is neutral when freshly prepared, has after a few hours a strongly alkaline reaction. It is also noticed that freshly prepared solutions of the carbinol do not show any fluorescence, but after keeping for some time the solutions, like the solution of the free base prepared from the iodide by silver oxide, are strongly fluorescent.*

The gradual change from the carbinol to the ammonium form of the pseudo-base was also followed by means of Hantzsch's method of conductivity measurements. The formation of an ammonium hydroxide from cotarnine and of carbinols from phenylmethyl-

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* The fluorescence in this and in many other cases is best seen by means of the illumination of the spark when the liquid is under examination in the Baly spectroscopic cell.

acridinium and other substituted ammonium hydroxides, has previously been investigated by Hantzsch (*Ber.*, 1899, **32**, 575, 3109) by this method.

In the following table the molecular conductivity of benziminazolol is given at 30° and at a dilution of $N/500$ over a period of five hours:

Time in hours.	Molecular conductivity.	Time in hours.	Molecular conductivity.
1	14·9	4	29·0
2	20·2	5	33·8
3	24·4		

After heating the solution for a short time on the water-bath, μ_{500} at 30° = 131. A solution of the ammonium base prepared from the iodide by silver oxide gave μ_{500} at 30° = 134·8.

It is found that when the conductivity of the "carbinol" solution is equal to that of the ammonium base prepared by the silver oxide method, the spectra of the two solutions are also identical. The gradual change of the carbinol into the ammonium base can thus be followed at the same time by conductivity and spectroscopic measurements.

Although the transformation of the carbinol into the ammonium form takes place slowly with water alone, it is immediately effected by the addition of hydrochloric acid to a freshly-made solution of the substance, the spectra of the solution becoming identical with those of the quaternary iodide and hydroxide. In this case, however, the quaternary chloride is produced, and can be isolated from the solution (O. Fischer and Rigaud, *Ber.*, 1902, **35**, 1258).

The conversion of the ammonium base into the carbinol is also easily followed by means of the spectroscope. On the addition of excess of a soluble base to a solution of either the quaternary salt or free base, the spectra which are obtained are identical with those of a freshly prepared solution of the carbinol (compare O. Fischer and Rigaud, *loc. cit.*).

In this case, however, the change takes place at once, if sufficient alkali is present, and in this respect differs from the reverse change of carbinol into free ammonium base which takes place slowly. If varying quantities of alkali are added, the change can be followed through all its stages.

It is found that in the case of these compounds, as in other cases, that considerably less alkali is required to effect the conversion of a given quantity of ammonium base into carbinol if the reaction is carried out in alcoholic rather than aqueous solution.

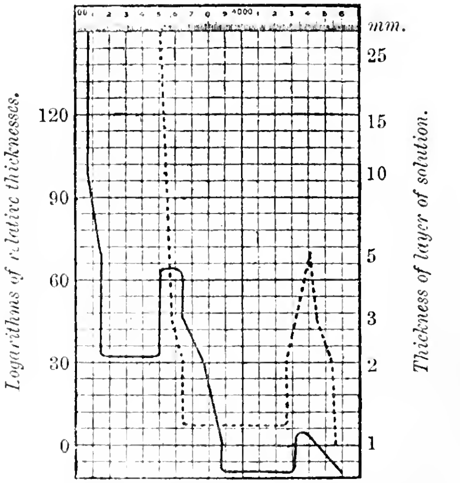
The absorption curves of the various solutions are shown in Fig. 1.

It appears from these results that the transference of the free azolium hydroxide into the carbinol is reversible, and that in this respect the case is analogous to that of cotarnine, which was the first case investigated by the spectroscopic method (Dobbie, Lauder, and Tinkler, Trans., 1903, **83**, 598).

No indication of the existence of a pseudo-cyanide was obtained in the case of these benziminazole derivatives, as no change in spectra is produced by the addition of potassium cyanide to the aqueous or alcoholic solution of the quaternary salt.

FIG. 1.

Scale of oscillation frequencies.

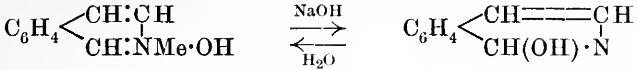


——— *Dimethylbenziminazolol in alcohol.*
- - - - - - *Dimethylbenziminazolium iodide in water.*
1 *mg.-mol. in* 500 *c.c.*

(b) iso*Quinoline Derivatives.*

(1) 1-*Hydroxy*-2-*methyl*-1 : 2-*dihydro*iso*quinoline*.—The chemical investigation of the carbinol–ammonium base isomerism in connexion with *iso*quinoline has recently been carried out by Decker (*J. pr. Chem.*, 1911, [ii], **84**, 425). He found that on shaking a solution of *iso*quinoline methiodide containing sodium hydroxide with benzene, and subsequent treatment of the benzene solution with water, a strongly alkaline solution was obtained. He supposed that by the action of the sodium hydroxide on the quaternary ammonium halide an equilibrium mixture of free ammonium base (VIII) and carbinol, 1-hydroxy-2-methyl-1 : 2-dihydro*iso*quinoline

(IX), was produced, and that the carbinol, which was extracted by benzene, was reconverted into the ammonium base by water:



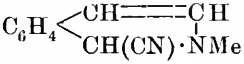
$$C_6H_4<\begin{array}{l}\mathrm{CH{:}CH}\\ \mathrm{CH{:}NMe\cdot OH}\end{array} \underset{H_2O}{\overset{NaOH}{\rightleftarrows}} C_6H_4<\begin{array}{l}\mathrm{CH{=}CH}\\ \mathrm{CH(OH)\cdot N}\end{array}$$

(VIII.) (IX.)

Evidence in support of this view is obtained by an examination of the absorption spectra of *iso*quinoline methiodide and its derivatives.

The following results were obtained in this connexion:

On the addition of potassium hydroxide to a dilute alcoholic solution of *iso*quinoline methiodide, a complete change in the spectra is produced. The same change is observed on the addition of potassium cyanide to the solution. It is therefore concluded that in the former case the pseudo-base or carbinol (IX) is produced, and in the latter that the solution contains the corresponding pseudo-cyanide (X):



$$C_6H_4<\begin{array}{l}\mathrm{CH{=}CH}\\ \mathrm{CH(CN)\cdot NMe}\end{array}$$

(X.)

Confirmation of this is obtained from the fact that the spectra of both solutions are in close agreement with those of Freund and Bode's 1:2-dimethyl-1:2-dihydro*iso*quinoline (XI), which is prepared by the action of magnesium methyl iodide on *iso*quinoline methiodide (*Ber.*, 1909, **42**, 1746):

$$C_6H_4<\begin{array}{l}\mathrm{CH{=}CH}\\ \mathrm{CHMe\cdot NMe}\end{array}$$

(XI.)

The absorption curves of these substances are shown in Fig. 2. It is interesting to note that this hydro-base (XI) is decomposed by hydrochloric acid. It would be expected that on the addition of hydrochloric acid to a solution of this hydro-base no great change in spectra would be produced. Such a solution, however, shows practically no absorption, and the original spectra are not reproduced on neutralisation of the acid.

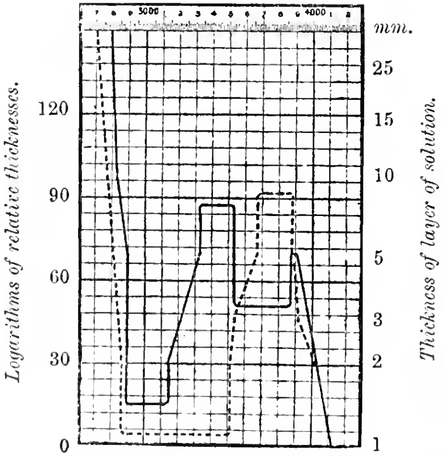
An aqueous solution of the ammonium base, prepared by the action of water on a benzene solution of the carbinol (IX) obtained by Decker's method, gives spectra which agree closely with those of the parent *iso*quinoline methiodide and with those of a solution containing the free ammonium base, prepared by the action of silver oxide on the quaternary halogen salt. It would therefore appear that water causes a reconversion of the carbinol into the ammonium base as suggested by Decker.

The reverse change of ammonium base into carbinol can also be followed by means of the spectroscope. By gradually increasing the amount of potassium hydroxide in a given aqueous solution of *iso*quinoline methiodide, the spectra more nearly approach those of 1:2-dimethyl-1:2-dihydro*iso*quinoline. This can only be explained by assuming that a greater proportion of the free ammonium base is converted into the carbinol by increasing the amount of alkali.

It was found that whereas in the case of the reduced substituted *iso*quinoline derivatives, cotarnine and hydrastinine, the conversion of the ammonium form into the carbinol form is practically complete in 2*N*-sodium hydroxide solution, the corresponding methyl *iso*quinolinium hydroxide requires a very much larger amount of free alkali to effect this transformation.

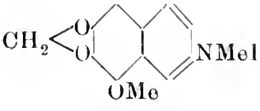
FIG. 2.

Scale of oscillation frequencies.



——— iso*Quinoline methiodide in alcohol*
(compare Hantzsch, *Ber.*, 1911, **44**, 1823).
- - - - - - *Dimethyldihydro*iso*quinoline in alcohol.*
1 *mg.-mol. in* 500 *c.c.*

(2) 1-*Hydroxy*-8-*methoxy*-6:7-*methylenedioxy*-2-*methyl*-1:2-*dihydro*iso*quinoline.*—The substituted *iso*quinoline derivative, tarconine methiodide (XII), which is prepared from narcotine by oxidation by means of iodine (Roser, *Annalen*, 1888, **245**, 316), differs only from cotarnine iodide in not having the 3:4-carbon atoms reduced:

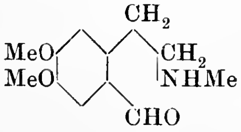


(XII.)

Bruns (*Arch. Pharm.*, 1905, **243**, 57) states that the ammonium base derived from tarconine methiodide has little tendency to react in the tautomeric aldehyde form, since no oxime or acetone derivative could be prepared, as are obtained in the case of cotarnine. In view, however, of the results obtained by the spectroscopic method in the case of other *iso*quinoline derivatives, it was expected that evidence would be obtained of the transformation of the ammonium base into the closed-chain carbinol, 1-hydroxy-8-methoxy-6 : 7-methylenedioxy-2-methyl-1 : 2-dihydro*iso*quinoline, and not into the corresponding open-chain aldehyde.

On the addition of potassium hydroxide to an alcoholic solution of tarconine methiodide, a complete change in spectra is produced. The two absorption bands of the salt 1/λ 3150 and 1/λ 3770 are replaced by one band 1/λ 3380. Since a similar change is produced by the addition of potassium cyanide to the solution, it is concluded that in the former case the carbinol is produced. On acidifying the potassium hydroxide solution, the spectra of the original salt are reproduced. The solution of the carbinol rapidly becomes strongly coloured.

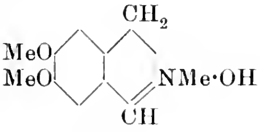
(3) 1-*Hydroxy*-6 : 7-*dimethoxy*-2-*methyltetrahydro*iso*quinoline.*—The carbinol–ammonium base isomerism as met with in the tetrahydro*iso*quinoline derivatives cotarnine and hydrastinine, has previously been investigated by the spectroscopic method (Dobbie, Lauder, and Tinkler, *loc. cit.*; and Dobbie and Tinkler, Trans., 1904, **85**, 1005). Since that time Pyman (Trans., 1909, **95**, 1266) in the course of an investigation on *iso*quinoline compounds has, however, described a new base and its derivatives closely related to cotarnine and hydrastinine. This new base, together with veratraldehyde, was obtained by the oxidation of laudanosine (*N*-methyltetrahydropapaverine), and from its analogy to cotarnine and hydrastinine is represented as an open-chain compound, 4 : 5-dimethoxy-2-β-methylaminoethylbenzaldehyde (XIII):



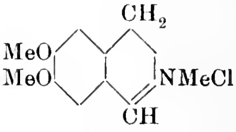
(XIII.)

Since, however, it has been shown in the case of cotarnine and hydrastinine by the spectroscopic method of investigation that these substances are more correctly represented as closed-chain carbinols than open-chain aldehydeamines, it appeared probable that the same would apply to this new base, as it differs only from hydrastinine in having two methoxy-groups instead of the methylenedioxy-group of the latter.

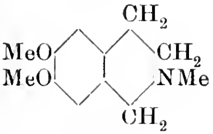
The base, like cotarnine and hydrastinine, is colourless, but gives rise to coloured salts of 6:7-dimethoxy-2-methyl-3:4-dihydro*iso*quinolinium hydroxide (XIV) by substitution. Of these the chloride (XV) is characteristic. A hydro-compound (XVI) and a pseudo-cyanide (XVII) can also be prepared from the base (Pyman, *loc. cit.*):



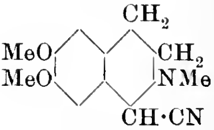
(XIV.)



(XV.)



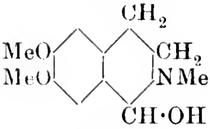
(XVI.)



(XVII.)

A further resemblance to cotarnine and hydrastinine is shown by the fact that the base gives a strongly alkaline solution in water (Pyman, *loc. cit.*).

If this base obtained from laudanosine is to be represented as the closed-chain carbinol, 1-hydroxy-6:7-dimethoxy-2-methyltetrahydro*iso*quinoline (XVIII), its absorption spectra in solvents such



(XVIII.)

as ether and chloroform should be identical with those of 6:7-dimethoxy-2-methyltetrahydro*iso*quinoline (XVI) and the corresponding cyano-compound (XVII), whilst if the alkalinity of the aqueous solution of the base is due to the formation of the free ammonium base (XIV), this would readily be detected by the agreement of the spectra with those of the parent salt (XV).

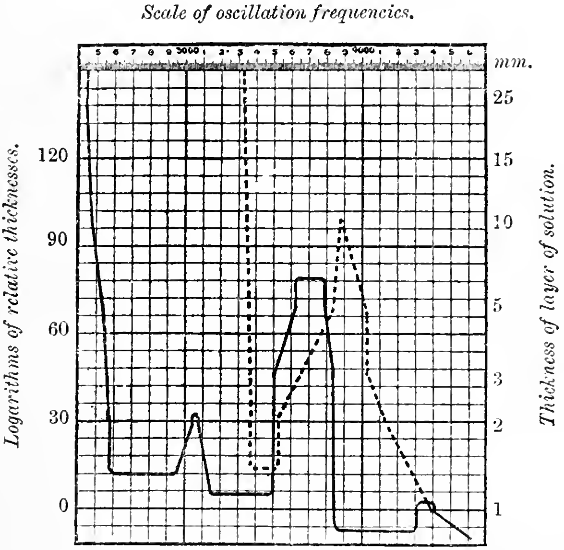
The results obtained from the spectroscopic examination of this base and its derivatives were as follows:

The spectra of ethereal and chloroform solutions of the base are identical with those of the corresponding hydro-compound (XVI) and with those of the cyano-compound (XVII) in chloroform. Since there is no reason for believing that either ether or chloroform produce any change in the constitution of the base, this agreement of spectra can only be explained by assigning to the substance the carbinol formula (XVIII).

The spectra of a solution of the base in alcohol, as in the corresponding cases of cotarnine and hydrastinine, show that the solvent causes a partial conversion into the ammonium form (XIV), as they can be reproduced by photographing the spectra of solutions of the hydro-compound and quaternary ammonium salt mixed in known proportions.

The spectra of dilute aqueous solutions of the base show that the substance is wholly converted into the ammonium form by water, as in this case the spectra are practically identical with those of the corresponding salt (Fig. 3). On the addition of alkali to either the alcoholic or aqueous solution of the base, the spectra obtained are identical with those of the base in ether or chloroform. The carbinol is therefore converted into the ammonium form by water or alcohol, but reconverted into the carbinol form on the addition of alkali to the solution.

FIG. 3.



———— 6 : 7-*Dimethoxy*-2-*methyl*-3 : 4-*dihydro*isoquinolinium *chloride.*
- - - - - - 6 : 7-*Dimethoxy*-2 *methyltetrahydro*isoquinoline.
1 *mg.-mol. in* 500 *c.c.*

Although the spectra of the cyano-compound in chloroform are identical with those of the hydro-compound, an alcoholic solution of the pseudo-cyanide gives spectra characteristic of a mixture of the pseudo- and true cyanides. It is probable that in this case, as in the case of hydrastinine, the alcohol causes a partial conversion of the pseudo-cyanide into the true salt. On the addition of potassium cyanide to the solution, the spectra become identical with those of the pseudo-cyanide in chloroform and of the hydro-compound.

It was found in connexion with the preparation of these compounds that the hydro-compound, which was prepared by Pyman by the action of sodium hydroxide on the free base, could also be prepared by the reduction of the chloride of the base, as in the case of cotarnine and hydrastinine.

The reduction was effected by means of zinc and sulphuric acid and also electrolytically. In the reduction by means of zinc the solution of the chloride, which is yellow and fluorescent, was treated with zinc and sulphuric acid, and the action allowed to proceed until the solution became colourless. Sodium hydroxide was then added, and the base extracted by means of ether.

In the electrolytic preparation the reduction was carried out in a Tafel reduction cell after the manner of the reduction of cotarnine and hydrastinine by Bandow and Wolffenstein (*Ber.*, 1898, **31**, 1578).

The author wishes to express his thanks to Mr. W. E. Garner, B.Sc., for carrying out the conductivity measurements recorded in this paper, and to the Research Fund Committee of the Chemical Society for a grant, by means of which some of the materials used in this investigation have been purchased.

THE UNIVERSITY,
BIRMINGHAM.

CXXXV.—*α-Hydroxyhippuric Acid and a New Test for Hippuric Acid.*

By PAUL HAAS.

IN the year 1892 Drechsel (*Ber. K. Sächs. Ges. Wiss. math. phys. Kl.*, 1892, **44**, 115) claimed to have obtained α-aminohippuric acid, $C_6H_5 \cdot CO \cdot NH \cdot CH(NH_2) \cdot CO_2H$, by benzoylating the cleavage products resulting from the acid hydrolysis of casein; he stated that on hydrolysis it yielded a well defined, crystalline solid, which from analysis appeared to be diaminoacetic acid, $CH(NH_2)_2 \cdot CO_2H$. Some doubt was subsequently cast on the identity of this latter substance owing to the fact that attempts by Klebs (*Zeitsch. physiol. Chem.*, 1894, **19**, 302) and later Sörensen (*Compt. rend. Lab. Carlsberg*, 1903, **6**, 1) to synthesise diaminoacetic acid were unsuccessful, the authors being unable to isolate any substance which could be identified with Drechsel's compound; furthermore, Willstätter (*Ber.*, 1902, **35**, 1379) on preparing methyl tetramethyldiaminoacetate, $CH(NMe_2)_2 \cdot CO_2Me$, found that this substance was an unstable oil boiling at 57—58°/12·5 mm., which readily reduced silver nitrate, and was decomposed by boiling aqueous alkali carbonates or hydroxides, and he therefore concluded that the stable substances described by Drechsel could not in reality have had the constitutions assigned to them.

As no experiments appeared to have been made with the view of synthesising Drechsel's benzoyl derivative, it was thought worth while attempting to prepare this substance by acting on hippuric acid with bromine and treating the resulting compound with ammonia; the method has, however, failed owing to the inability to isolate α-bromohippuric acid; that this substance is, however, at least temporarily formed would appear probable from the fact that on pouring the product of the action of bromine and red phosphorus on hippuric acid into water, the corresponding α-hydroxyhippuric acid is formed; on trying to prepare the α-amino-acid by pouring the reaction product into ammonia, the substance was either hydrolysed to benzamide or else converted into the amide of hydroxyhippuric acid,

$$C_6H_5 \cdot CO \cdot NH \cdot CH(OH) \cdot CO \cdot NH_2.$$

Attempts to isolate the α-bromo-acid by pouring the brominated mixture into anhydrous formic acid likewise failed, and resulted only in the formation of α-hydroxy-acid.

That this hydroxy-acid is the α-substituted hippuric acid is shown by its behaviour on hydrolysis; unlike hippuric acid, it is very readily decomposed by acids or alkalis, the nitrogen remaining attached to the benzoyl group giving benzamide and glyoxylic acid, according to the equation:

$$C_6H_5 \cdot CO \cdot NH \cdot CH(OH) \cdot CO_2H + H_2O = C_6H_5 \cdot CO \cdot NH_2 + CH(OH)_2 \cdot CO_2H.$$

This hydrolysis takes place so readily that the mere addition of concentrated sulphuric acid to an aqueous solution of the hydroxy-acid containing a little protein, at once produces an intense violet colour due to the liberation of glyoxylic acid.

If bromine is allowed to act directly on a mixture of hippuric acid and red phosphorus, the reaction is violent, and a brown decomposed mass results; by suspending the hippuric acid and red phosphorus in carbon tetrachloride, and adding to this a solution of bromine in the same solvent, the reaction may be moderated, but even then care must be taken not to heat the mixture too long or a considerable amount of decomposition will ensue.

Test for Hippuric Acid.—When carried out as follows, the conversion of hippuric acid into hydroxyhippuric acid may be employed as a delicate test for the former substance. A small quantity of finely powdered hippuric acid, together with a little red phosphorus, is placed in a test-tube, and just covered with two or three drops of chloroform; bromine is then added, drop by drop, until there is a slight excess, and the mixture is gently warmed until a clear red liquid results; a few c.c. of water are thereupon added, and the mixture is boiled until a colourless liquid, free from bromine or chloroform, remains; after cooling, a little protein solution (Witte peptone or egg albumen) is added, and concentrated sulphuric acid is carefully poured down the side of the test-tube; after a short time a purple or violet colour develops above the sulphuric acid, and on careful agitation extends over the whole solution.

EXPERIMENTAL.

Twenty grams (3 mols.) of finely * powdered hippuric acid and 1·2 grams (1 atom) of red phosphorus were thoroughly ground together and suspended in 60 c.c. of dry carbon tetrachloride contained in a retort attached to a reflux condenser; to this mixture was added in portions a solution of 36 grams (12 atoms) of bromine in 40 c.c. of carbon tetrachloride; about half of this solution was run in fairly rapidly, the remainder being added during the course of two hours. The retort was kept just warm by keeping it over a very gently simmering water-bath, the heating being continued for about one and a-half hours after the addition of the last quantity of bromine. After cooling, the pale red supernatant liquid was poured off, and the yellowish-brown solid remaining was ground with 20 c.c. of cold water; there was a slight rise of temperature, and the substance softened somewhat, but after a short time it hardened again, leaving a pale yellow solid. This substance was then crystallised by dissolving it in three times its weight of boiling water, when on cooling 11 grams of a cream-coloured solid separated out. For further purification the substance was boiled with benzene, in order to extract a small quantity of benzamide which is usually present, and again crystallised from water:

0·1345 gave 0·2723 CO_2 and 0·0634 H_2O. C = 55·21; H = 5·23.
0·1226 „ 7·8 c.c. N_2 at 12° and 750 mm. N = 7·45.
0·1898, by Kjeldahl's method, required 10 c.c. $N/10$-HCl. N = 7·37.

$C_9H_9O_4N$ requires C = 55·38; H = 4·61; N = 7·18 per cent.

α-Hydroxyhippuric acid, $C_6H_5\cdot CO\cdot NH\cdot CH(OH)\cdot CO_2H$, is a

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* The substance was passed through an 80-mesh sieve.

colourless solid with a faint aromatic odour; it crystallises from aqueous solution in warty aggregates or in transparent, glistening plates; it has no sharp melting point, but when heated in a capillary tube it softens and melts with frothing at about 145—150°, and then solidifies again; at about 180° it darkens, and finally melts with decomposition at about 208—213°; it is readily soluble in hot alcohol, but only sparingly so in acetone, and is insoluble in chloroform, benzene, ethyl acetate, or light petroleum.

A molecular-weight determination by titration gave the following numbers:

0·1513 required for neutralisation 7·69 c.c. *N*/10-KOH. M.W. = 196·5.

$C_9H_9O_4N$ requires M.W. = 195.

The *silver* salt prepared by adding an excess of silver nitrate to a carefully neutralised solution of the acid is decomposed almost immediately on the addition of ammonia with formation of a silver mirror, owing to the liberation of glyoxylic acid by the hydrolytic action of the ammonia:

0·1226 gave 0·0442 Ag. Ag = 36·05.

$C_9H_8O_4NAg$ requires Ag = 35·76 per cent.

The *calcium* salt was obtained by adding powdered calcium carbonate to a boiling aqueous solution of the acid until effervescence ceased; it separated from the filtered solution in transparent prisms:

0·5300 gave 0·0709 CaO. Ca = 9·55.

$(C_9H_8O_4N)_2Ca$ requires Ca = 9·34 per cent.

The *methyl* ester obtained by heating the silver salt with methyl iodide in benzene solution crystallises from a mixture of benzene and light petroleum in slender plates, and melts at 114—116°; it is soluble in the ordinary organic solvents, and, unlike most esters, is also soluble in hot water; it has a faint aromatic odour somewhat resembling that of methyl salicylate, with which it is isomeric:

0·1821, by Kjeldahl's method, required 8·67 c.c. *N*/10-HCl. N = 6·66.

$C_{10}H_{11}O_4N$ requires N = 6·69 per cent.

The *amide*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH(OH){\cdot}CO{\cdot}NH_2$, was prepared as follows: Hippuric acid was treated with bromine in carbon tetrachloride solution, as described under the preparation of α-hydroxyhippuric acid (p. 1256); when the reaction was completed, the carbon tetrachloride was poured off, and the brown solid remaining was dried in a vacuum; it was then powdered, and after being washed two or three times with dry ether it was suspended in this medium and saturated with dry ammonia; the ether was then evaporated in a vacuum, and the pale yellow solid residue crystallised from hot water:

0·1192 gave 0·2421 CO_2 and 0·0586 H_2O. C=55·39; H=5·45.
0·1166 „ 0·2374 CO_2 „ 0·0558 H_2O. C=55·52; H=5·31.
0·1500, by Kjeldahl's method, required 15·7 c.c. *N*/10-HCl. N=14·66.

$C_9H_{10}O_3N_2$ requires C=55·67; H=5·15; N=14·43 per cent.

a-Hydroxyhippuramide is sparingly soluble in hot water, and crystallises from this solvent in slender, colourless needles melting and decomposing at 170—171°; it is insoluble in the ordinary organic solvents.

The numbers obtained by analysis agree equally well for the benzoyl derivative of diaminoacetic acid and for the amide of hydroxyhippuric acid, since these two substances are isomeric, but the compound here described must be the amide, since it gives no silver salt or platinichloride.

Hydrolysis of Hydroxyhippuric Acid.

When warmed with an aqueous solution of ammonia, hydroxyhippuric acid is readily hydrolysed, giving an almost quantitative yield of benzamide; thus 1 gram of hydroxyhippuric acid, when dissolved in 10 c.c. of dilute ammonia solution and warmed for a short time over a water-bath, deposited on cooling 0·5 gram of glistening plates, which after crystallisation from a solution of ammonia melted at 128°:

0·1530, by Kjeldahl's method, required 12·8 c.c. *N*/10-HCl. N=11·70.

C_7H_7ON requires N=11·57 per cent.

Similarly, when boiled with hydrochloric acid, hydroxyhippuric acid is decomposed into benzamide and glyoxylic acid; the latter substance was identified by conversion into its phenylhydrazone, which melted at 139°.

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CXXXVI.—*The Refractivity of Sulphur in Various Aliphatic Compounds.*

By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

IN recent years Auwers and Eisenlohr (*Ber.*, 1910, **43**, 806, 827; *J. pr. Chem.*, 1911, [ii], **84**, 1, 37) and Eisenlohr (*Zeitsch. physikal. Chem.*, 1910, **75**, 585; 1912, **79**, 129) have published a number of papers dealing with the refractive constants of the various elements occurring in organic compounds, and especially with the influence of the method of linking on the value of these constants. In one paper (*Ber.*, 1911, **44**, 3188) Eisenlohr has dealt especially with the effect of the conjugation of elements possessing auxiliary valencies with a double bond in compounds containing halogens, nitrogen, phosphorus, and sulphur, and has referred to the subject again in a paper on the refractive constants of nitrogen (*Zeitsch. physikal. Chem.*, 1912, **79**, 129). The conclusions arrived at are summarised as follows:

"The unsaturated character of auxiliary valencies is shown by the optical exaltation produced when they are in a conjugated position to a double bond. The magnitude of this exaltation is usually not large, and is considerably less than that caused by conjugated double bond systems; it varies according to the extent to which the element in question is saturated."

"Disturbing substituted groups introduced into such conjugations depress the exaltation, and when two or more disturbing groups are introduced the exaltation becomes a depression."

"Crossed conjugations in which auxiliary valencies take part do not behave optically in an analogous manner to the corresponding double bond systems. In the former case there is a considerable lessening of the exaltation."

"The optical influence of the auxiliary valencies in an incompletely saturated atom is most marked in the refraction value, less so in the dispersion value."

These conclusions have been adversely criticised by Auwers (*Ber.*, 1911, **44**, 3679), but Eisenlohr (*Zeitsch. physikal. Chem.*, 1912, **79**, 130, footnote) reserves his reply until he has collected more data, "especially with respect to compounds containing sulphur."

In various papers (Trans., 1908, **93**, 1645; 1909, **95**, 1050) we have described the preparation of a number of esters of dithio-acids, and some considerable time ago the densities and refractive indices of these esters were measured; but the results were not published owing to the pressure of other work. As we did not know to what extent Dr. Eisenlohr had proceeded in his collection of data for sulphur compounds, we communicated with him, offering him our results for incorporation with his own. He suggested, however, that as it may be some time before his thesis is ready, we should publish our data, and at the same time he very kindly forwarded some measurements made by himself on sulphur compounds prepared by Prof. Delépine, of Paris. We desire to express our great indebtedness to him in this respect.

The measurements we have ourselves made are given in the following tables. The densities and refractive indices were deter-

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Dimethyl dithiodiglycollate, $S_2(CH_2{\cdot}CO_2Me)_2$	Diethyl dithiodiglycollate, $S_2(CH_2{\cdot}CO_2Et)_2$.	Diethyl α-dithiodilactylate, $S_2(CHMe{\cdot}CO_2Et)_2$.	Diethyl β-dithiodilactylate, $S_2(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$.	Diethyl α-dithiodibutyrate, $S_2(CHEt{\cdot}CO_2Et)_2$.	Diethyl α-dithiodi*iso*butyrate, $S_2(CMe_2{\cdot}CO_2Et)_2$.	Diethyl α-dithiodi*iso*valerate, $S_2[CH(CHMe_2){\cdot}CO_2Et]_2$.
Mol. wt. ...	210·2	238·2	266·3	266·3	294·3	294·3	322·3
D^{16}_{4}	1·2905	1·2036	1·1398	1·1532	1·0992	1·1065	1·0680
D^{25}_{4}	1·2809	1·1945	1·1308	1·1444	1·0909	1·0980	1·0602
Mol. vol. at 16°	162·9	197·9	233·6	230·9	267·7	266·0	301·8
Mol. vol. at 25°	164·1	199 4	235·5	232·7	269·8	268·0	304·0
n^{16}_{α}	1·51171	1·49760	1·48907	1·49337	1·48448	1·48610	1·48129
n^{25}_{α}	1·50792	1·49377	1·48508	1·48967	1·48107	1·48251	1·47771
n^{16}_{D}	1·51517	1·50085	1·49222	1·49650	1·48753	1·48926	1·48423
n^{16}_{D} (calc.) ...	(1·51526)	(1·50089)	(1·49225)	(1·49652)	(1·48763)	(1·48928)	(1·48432)
n^{25}_{D}	1·51137	1·49701	1·48822	1·49282	1·48412	1·48567	1·48076
n^{25}_{D} (calc.) ...	(1·51145)	(1·49709)	(1·48829)	(1 49280)	(1·48413)	(1·48567)	(1·48069)
n^{16}_{β}	1·52388	1·50887	1·49995	1·50415	1·49524	1·49698	1·49166
n^{25}_{β}	1·51999	1·50515	1·49606	1·50038	1·49155	1·49331	1·48791
n^{16}_{γ} (calc.) ...	(1·53074)	(1·51523)	(1·50608)	(1·51022)	(1·50131)	(1·50311)	(1·49751)
n^{25}_{γ} (calc.) ...	(1·52680)	(1·51156)	(1·50225)	(1·50642)	(1·49746)	(1·49940)	(1·49366)
M^{16}_{α}	48·85	57·97	67·44	67·15	76·66	76·38	85·93
M^{25}_{α}	48·91	58·03	67·50	67·24	76·78	76·48	86·01
Mean value for M_{α} ...	**48·88**	**58·00**	**67·47**	**67·19**	**76·72**	**76·43**	**85·97**
M^{16}_{D}	49·13	58·29	67·81	67·51	77·07	76·80	86·37
M^{25}_{D}	49·19	58·36	67·88	67·60	77·20	76·91	86·48
Mean value for M_{D} ...	**49·16**	**58·32**	**67·84**	**67·55**	**77·13**	**76·85**	**86·42**
M^{16}_{β}	49·83	59·08	68·71	68·39	78·11	77·83	87·50
M^{25}_{β}	49·89	59·16	68·80	68·48	78·21	77·94	87·57
Mean value for M_{β} ...	**49·86**	**59·12**	**68·75**	**68·43**	**78·16**	**77·88**	**87·53**
M^{16}_{γ}	(50·37)	(59·70)	(69·42)	(69·09)	(78·92)	(78·64)	(88·39)
M^{25}_{γ}	(50·43)	(59·80)	(69·53)	(69·18)	(79·00)	(78·75)	(88·45)
Mean value for M_{γ} ...	**(50·40)**	**(59·75)**	**(69·47)**	**(69·13)**	**(78·96)**	**(78·69)**	**(88·42)**

mined both at 16° and 25°. Before each measurement the ester, which was analytically pure, was freshly distilled under diminished pressure. In the case of diethyl **α**-dithiodilactylate we convinced ourselves that one distillation was sufficient by carrying out a second distillation, and redetermining the refractive indices for various wave-lengths; the values found were exactly the same as after the first distillation. The other esters were distilled once only, since they are very objectionable, not only to the actual investigators while handling them, but also to other persons who may be in the same building.

The molecular refractivities have been calculated according to the n^2 formula of Lorentz and Lorenz, and show a very good agreement between the values obtained at 16° and 25°. It should be mentioned, however, that an even better agreement is obtained when the formula of Gladstone and Dale, namely, $M(n-1)/d$, is used; for example, in the case of diethyl **β**-dithiodilactylate the molecular refractivities for the H_α line are then 113·92 and 113·94 at 16° and 25° respectively.

Unfortunately, when the measurements were carried out, only the refractive indices for the H_α, D, and H_β lines were determined. It is, however, desirable to know the values for the H_γ line, and these we have obtained by calculation from Cauchy's formula, $n = A + B/\lambda^2$, since, as has already been mentioned, the dithio-esters are so objectionable to handle. To test if this calculation is of any value in this particular case, we have calculated n_D from the values for n_α and n_β, both at 16° and 25°, and a glance at the table will show that the agreement between the experimental and calculated values is an exceedingly good one. We therefore feel justified in giving the values for n_γ printed in the table; the calculated values are distinguished, however, by being bracketed.

The atomic refractivity (r) of sulphur, as calculated from the above values, is given in the following table. The values for carbon, hydrogen, and oxygen used in the calculations are those given by Auwers and Eisenlohr (*loc. cit.*). The figures, 1, 2, etc., refer to the same compounds as in the previous table.

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	Mean value.
r_α	8·04	7·99	8·12	7·98	8·15	8·01	8·18	**8·07**
r_D	8·09	8·05	8·19	8·05	8·22	8·08	8·25	**8·13**
r_β	8·26	8·22	8·37	8·21	8·40	8·26	8·42	**8·31**
r_γ	(8·38)	(8·35)	(8·50)	(8·33)	(8·53)	(8·39)	(8·55)	**(8·43)**

The dithio-esters in question do not contain an auxiliary valency in conjugation with a double bond, so that the refractivities of the sulphur atom should be comparable with those deduced from ethyl disulphide, the molecular refractivity of which has been determined by Nasini (*Ber.*, 1882, **15**, 2878). In order to make a proper comparison, however, it has been found necessary to recalculate the molecular refractivity, using the modern atomic weights, and expressing the molecular weight to four significant figures, in accordance with the method adopted by Auwers and Eisenlohr. For convenience of reference to other investigators, it will be necessary to give the recalculated data, not only of ethyl disulphide, but also of the other compounds discussed in the sequel. From space considerations the whole of the recalculated data are given together in the following table; also, in order to obtain an idea of the agreement obtained in the various groups of compounds, the atomic refractivities for one atom of sulphur are included, as deduced from the molecular refractivities, no account being taken of the various ways in which the sulphur atoms are linked.

Compound and formula.	Mol. wt.	M_{α}.	M_{D}.	M_{β}.	M_{γ}.	r_{α}.	r_{D}.	r_{β}.	r_{γ}.	Authority.
Ethyl mercaptan, EtSH :	62·12	19·04	19·15	19·43	19·68	7·66	7·70	7·86	8·02	Nasini[1]
i-Butyl mercaptan, $C_4H_9{\cdot}SH$:	90·15	28·19	28·35	28·74	29·05	7·62	7·67	7·84	7·97	,,
i-Amyl mercaptan, $C_5H_{11}{\cdot}SH$:	104·2	32·78	32·98	33·37	33·74	7·61	7·69	7·80	7·95	,,
Ethyl sulphide, Et_2S :	90·15	28·40	28·56	28·95	—	7·80	7·87	8·03	8·15	Brühl[2]
		28·37	28·53	28·91	29·24					Nasini[1]
i-Amyl sulphide, $(C_5H_{11})_2S$:	174·2	55·49	55·78	56·47	57·06	7·33	7·40	7·56	7·71	,,
Allyl sulphide, $(C_3H_5)_2S$:	114·1	36·76	37·01	37·67	38·21	7·99	8·04	8·24	8·41	,,
Acetal sulphide, $C_{12}H_{26}O_4S$:	266·3	71·68	72·19	—	—	7·76	8·00	—	—	Smiles & Clarke[3]
Ethyl disulphide, Et_2S_2 :	122·2	36·39	36·59	37·19	37·67	7·90	7·96	8·14	8·29	Nasini[1]
Methyl thiocyanate, MeSCN :	73·17	18·92	19·02	19·31	19·54	7·72	7·77	7·93	8·01	Nasini & Scala[4]
Ethyl thiocyanate, EtSCN :	87·12	23·79	23·93	24·27	—	7·99	8·06	8·23	—	,, ,,
Methyl thiocarbimide, MeNCS :	73·17	20·82	21·00	21·42	—	8·98	9·09	9·32	—	,, ,,
Ethyl thiocarbimide, EtNCS :	87·12	26·04	26·25	26·77	—	9·60	9·72	10·00	—	,, ,,
Allyl thiocarbimide, $C_3H_5{\cdot}NCS$:	99·12	29·75	30·06	30·67	—	9·25	9·38	9·62	9·87	,, ,,
		29·82	30·07	30·64	31·20					Berliner[5]
Ethyl thioncarbonate, $CS(OEt)_2$:	134·1	—	35·63	—	—	—	9·25	—	—	Wiedemann[6]
Methyl methyliminodithiolcarbonate, $MeN{:}C(SMe)_2$:	135·2	38·91	39·20	39·90	40·58	7·84	7·92	8·11	8·32	Eisenlohr[7]
Ethyl methyliminodithiolcarbonate, $MeN{:}C(SEt)_2$:	163·3	48·47	48·81	49·64	50·36	8·02	8·11	8·32	8·50	,,
Methyl ethyliminodithiolcarbonate, $EtN{:}C(SMe)_2$:	149·2	43·75	44·06	44·82	45·51	7·96	8·04	8·24	8·43	,,
Methyl dithiolcarbonate, $CO(SMe)_2$:	122·2	32·28	32·53	33·16	33·46	8·15	8·23	8·45	8·53	,,
Ethyl dithiolcarbonate, $CO(SEt)_2$:	150·2	—	42·34	—	—	—	8·52	—	—	Wiedemann[6]

Compound and formula.									
Ethyl thiolcarbonate, $CO(OEt)(SEt)$:									
Mol. wt.	M_{α}.	M_{D}.	M_{β}.	M_{γ}.	r_{α}.	r_{D}.	r_{β}.	r_{γ}.	Authority.
134·1	—	35·13	—	—	—	8·19	—	—	Wiedemann[6]
Methyl methylxanthate, $CS(SMe)(OMe)$:									
118·2	34·24	34·46	35·08	35·61	9·40	9·43	9·71	9·91	Eisenlohr[7]
Methyl ethylxanthate, $CS(SMe)(OEt)$:									
136·2	38·21	38·56	39·50	—	9·09	9·22	9·59	—	Nasini & Scala[8]
Methyl propylxanthate, $CS(SMe)(OPr^{\alpha})$:									
150·2	42·80	43·17	44·16	—	9·05	9·18	9·55	9·80	,, ,,
	42·67	43·03	44·03	44·82					Eisenlohr[7]
Ethyl ethylxanthate, $CS(SEt)(OEt)$:									
150·2	42·19	43·35	44·33	—	8·78	9·31	9·67	—	Nasini & Scala[8]
Ethyl propylxanthate, $CS(SEt)(OPr^{\alpha})$:									
164·2	47·63	48·01	49·06	—	9·20	9·33	9·70	—	,, ,,
Ethyl dithiothioncarbonate, $S_2(CS{\cdot}OEt)_2$:									
242·4	67·21	67·92	69·90	—	9·63	9·78	10·20	—	,, ,,
Propyl dithiothioncarbonate, $S_2(CS{\cdot}OPr^{\alpha})_2$:									
270·4	76·58	77·34	79·43	—	9·67	9·83	10·25	—	,, ,,
Methyl dipropylthionthiolcarbamate, $CS(SMe)(NPr^{\alpha}_2)$:									
191·3	59·19	59·72	61·07	62·32	9·42	9·59	10·02	10·55	Eisenlohr[7]

[1] Nasini, *Ber.*, 1882, **15**, 2878.

[2] Brühl, *Zeitsch. physikal. Chem.*, 1897, **22**, 388.

[3] Smiles and Clarke, Trans., 1909, **95**, 992.

[4] Nasini and Scala, *Gazzetta*, 1887, **17**, 67.

[5] Berliner, *Inaug. Diss. Breslau.*

[6] Wiedemann, *J. pr. Chem.*, 1872, [ii], **6**, 433.

[7] Eisenlohr: private communication to the authors. The compounds were prepared by Prof. Delépine.

[8] Nasini and Scala, *Gazzetta*, 1887, **17**, 72.

The values for the atomic refractivities of sulphur in ethyl disulphide are seen to be in approximate agreement with those obtained from the dithio-esters. The mean values resulting from all the disulphide compounds are:

$$r_{\alpha} = 8{\cdot}05\,; \qquad r_{D} = 8{\cdot}11\,; \qquad r_{\beta} = 8{\cdot}28\,; \qquad r_{\gamma} = (8{\cdot}41).$$

General Discussion of the Atomic Refractivity of Sulphur.

Mercaptans.

The values for the various mercaptans are in very close agreement, the mean values being:

	r_{α}.	r_{D}.	r_{β}.	r_{γ}.	$r_{\beta} - r_{\alpha}$.	$r_{\gamma} - r_{\alpha}$.
C—**S**—H	7·63	7·69	7·83	7·98	0·20	0·35

Sulphides.

A comparison of the values obtained from *i*-amyl sulphide with those resulting from the other compounds seems to indicate that they are abnormally low, and should be neglected in taking the average. Justification for neglecting them may be found in the fact that the values deduced from *i*-amyl mercaptan are in very good agreement with those deduced from the other mercaptans.

Measurements have been made on ethyl sulphide by two observers, Brühl and Nasini, and the results are in very close agreement. Nevertheless, in taking the mean value of the atomic refractivities, double weight has not been attached to these results, since the confirmation of Nasini's work by Brühl would indicate that Nasini's values for allyl sulphide are correct. It may be objected that this conclusion is not valid, owing to the abnormally low values obtained for *i*-amyl sulphide, which are also due to Nasini. There is, however, something inexplicable in the results for *i*-amyl sulphide, since in other cases where Nasini's work has been duplicated by other observers, for example, in the cases of allylthiocarbimide and methyl propylxanthate, very good agreement has been obtained.

It is noteworthy that acetal sulphide gives values agreeing with those obtained from the simpler sulphides.

The mean values are:

	r_α.	r_D.	r_β.	r_γ.	$r_\beta - r_\alpha$.	$r_\gamma - r_\alpha$.
C—**S**—C	7·85	7·97	8·13	8·28	0·28	0·43

There is thus an exaltation of the values for the atomic refractivity over those deduced from the mercaptans. This is in accordance with the results obtained for nitrogen (compare Eisenlohr, *Zeitsch. physikal. Chem.*, 1912, **79**, 129), the atomic refractivity of which in primary amines is less than in secondary amines, and still less than in tertiary amines, the replacement of hydrogen by an alkyl group increasing the refractivity.

Thiocyanates.

The values for nitrogen used in the calculations are those given by Eisenlohr (*loc. cit.*), as deduced from an examination of the aliphatic nitriles. Since the linkings of the sulphur are the same as in the sulphides, and the triple bond in the nitrile group is allowed for in the value used for the atomic refractivity of nitrogen, one would expect the values for the sulphur to be approximately the same as in the sulphides. That this is so is shown by the following mean values:

	r_α	r_D.	r_β	r_γ.	$r_\beta - r_\alpha$.	$r_\gamma - r_\alpha$.
C—**S**—CN..............	7·85	7·91	8·08	?	0·23	?

Disulphides.

The mean values for the atomic refractivity and dispersion are, as already given:

	r_α.	r_D.	r_β.	r_γ.	$r_\beta - r_\alpha$.	$r_\gamma - r_\alpha$
C—**S**—S—C	8·05	8·11	8·28	(8·41)	0·23	(0·36)

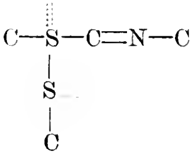
Since these values are derived from a study of eight different disulphides, they indicate that in these compounds the refractivity of sulphur is undoubtedly somewhat higher than in the mercaptans and sulphides. This increase in refractivity may be ascribed to the conjugation of the auxiliary valencies of the two sulphur atoms.

Brühl (*Ber.*, 1907, **40**, 1155) has found that conjugated nitrogen atoms in the hydrazines, $H_2N\cdot NH_2$, do not give rise to any appreciable exaltation. Eisenlohr (*Ber.*, 1911, **44**, 3202) states that the same holds for the aliphatic disulphides compared with the sulphides, and hence draws the conclusion that the conjugated auxiliary valencies of one and the same element have no exalting effect. In view of the above results it seems necessary to modify this conclusion in the case of the disulphides.

The dispersion values are of the same order as for the sulphides and mercaptans.

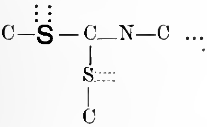
Alkyliminothiolcarbonates.

In these compounds there is a crossed conjugation between the auxiliary valencies of the sulphur and the double bond between the carbon and nitrogen, as may be seen by writing the formula thus:



$$\mathrm{C{-}}\underset{\substack{|\\ \mathrm{S}\\ |\\ \mathrm{C}}}{\overset{\vdots}{\mathrm{S}}}\mathrm{{-}C{=}N{-}C}$$

Comparison of the following mean values with the values deduced from the disulphides shows that the atomic refractivity of the sulphur is approximately the same as in the disulphides:



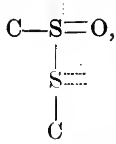
$$\mathrm{C{-}}\underset{\substack{|\\ \mathrm{S}\cdots\\ |\\ \mathrm{C}}}{\overset{\vdots\,\vdots}{\mathbf{S}}}\mathrm{{-}C{-}N{-}C}\ \ldots$$

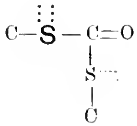
	r_{α}.	r_{D}.	r_{β}.	r_{γ}.	$r_{\beta}-r_{\alpha}$.	$r_{\gamma}-r_{\alpha}$.
...	7·94	8·02	8·26	8·42	0·32	0·48

Complicated conjugations of this kind have not yet been studied by Eisenlohr (compare footnote, *Ber.*, 1911, **44**, 3207), so that they have not been included in the generalisations given at the commencement of this paper. The conclusion may be drawn that such crossed conjugations behave similarly to the simple conjugation between two atoms of the same element possessing auxiliary valencies, that is, the relation is analogous to that existing between simple and crossed conjugations of carbon atoms.

The dispersion values are of the same order as in the sulphides.

Dithiolcarbonates.

In these compounds also there is a crossed conjugation similar to that considered in the previous case, namely,  $C-\underset{\underset{\underset{\underset{\displaystyle C}{|}}{S=}}{|}}{S}=O$, and in agreement therewith the values obtained for the atomic refractivity are of the same order as those for the single conjugation in the disulphides. In taking the mean values, the figure for ethyl dithiolcarbonate has been neglected, as it is obviously too high:

	r_α.	r_D.	r_β.	r_γ.	$r_\beta - r_\alpha$.	$r_\gamma - r_\alpha$.
 $C-\ddot{S}-\underset{\underset{\underset{\underset{\displaystyle C}{|}}{S}}{|}}{C}=O$	8·15	8·21	8·45	8·53	0·30	0·38

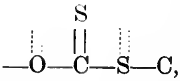
Thiocarbimides.

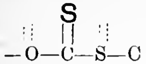
These compounds contain doubly linked sulphur, which, from analogy to carbon, oxygen, and nitrogen, should give a considerable exaltation in the value for the atomic refractivity. The following mean values are in agreement with this, although it will be noticed that the individual values for the various thiocarbimides are not in very good agreement with each other:

	r_α.	r_D.	r_β.	r_γ.	$r_\beta - r_\alpha$.	$r_\gamma - r_\alpha$.
S=CN	9·28	9·40	9·65	9·87	0·37	0·59

No definite conclusions can be drawn as to whether the dispersion value is normal or not, although apparently there is a slight exaltation. The value for S= is also in approximate agreement with that deduced from ethyl thioncarbonate (vide table).

Xanthates.

These compounds contain the linking  $-O-\overset{\overset{\displaystyle S}{\|}}{C}-S-C$, that is, conjugation of auxiliary valencies of sulphur and oxygen with doubly linked carbon. The value deduced for S= should, from analogy to the acid amides, where there is a conjugation between doubly linked oxygen and the auxiliary valencies of nitrogen, show an exaltation over that derived from the thiocarbimides. The following mean values are in agreement with this, and show, at the same time, that there is a considerable exaltation in the dispersion values.



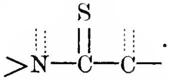
$-\mathrm{O}-\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}-\mathrm{S}-\mathrm{C}$ ....

r_{α}.	r_{D}.	r_{β}.	r_{γ}.	$r_{\beta}-r_{\alpha}$.	$r_{\gamma}-r_{\alpha}$.
10·52	10·64	11·16	11·43	0·64	0·91

In deducing the values for $\mathrm{S}=$ in these compounds, the value of 2S was calculated in the usual manner from the molecular refractivities, and then diminished by the value for C—S—C. The value of r_{α} for ethyl ethylxanthate has been neglected in taking the average, as it is obviously too low.

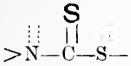
Methyl Dipropylthionthiolcarbamate.

In this compound the relations are similar to those in the xanthates, there being a conjugation of the auxiliary valencies of nitrogen and sulphur with those of doubly linked carbon, namely,



$>\mathrm{N}-\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}-\mathrm{C}-$.

Also, since the unsaturation of nitrogen is more marked than that of oxygen, the exaltation should be greater than in the xanthates, which is in accordance with the following figures:



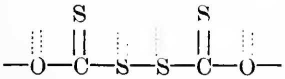
$>\mathrm{N}-\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}-\mathrm{S}-$ ....

r_{α}.	r_{D}.	r_{β}.	r_{γ}.	$r_{\beta}-r_{\alpha}$.	$r_{\gamma}-r_{\alpha}$.
10·99	11·21	11·92	12·63	0·93	1·64

The much greater exaltation in the dispersion values is very noticeable. The values for $\mathrm{S}=$ were obtained by subtracting the values for C—S—C from those deduced for the two sulphur atoms present.

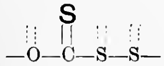
Dithiothioncarbonates.

The formula



$-\mathrm{O}-\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}-\mathrm{S}-\mathrm{S}-\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-$

shows that in these compounds there is an increased conjugation of auxiliary valencies over that existing in the xanthates, which would probably lead to a further exaltation in the values for $\mathrm{S}=$. The following mean values are in agreement with this, and indicate, at the same time, that there is also a very considerable exaltation in the dispersion value:



$-\mathrm{O}-\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}-\mathrm{S}-\mathrm{S}-$ ......

r_{α}.	r_{D}.	r_{β}.	r_{γ}.	$r_{\beta}-r_{\alpha}$.	$r_{\gamma}-r_{\alpha}$.
11·25	11·50	12·17	—	0·92	—

The value for $\mathrm{S}=$ was deduced by subtracting the value for —S—S— from that deduced for 4S in these compounds, and then dividing by two.

The above results may be looked upon as affording considerable support to, and to some extent as amplifying, Eisenlohr's generalisations on the optical effect of auxiliary valencies. The noteworthy difference is in connexion with the dispersion values obtained for compounds containing doubly linked sulphur in conjugation with auxiliary valencies; these show a considerable exaltation, just as do the atomic refractivities.

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CXXXVII.—*Morphotropic Relationships between Racemic Compounds and their Optically Active Components.*

By George Jerusalem.

In accordance with the results obtained by Kipping and Pope (Trans., 1897, **71**, 989; 1899, **75**, 36), crystalline externally compensated substances may occur, not only as mechanical mixtures of the two components or as true racemic compounds, but also as "pseudoracemic" compounds. Pseudoracemic substances exhibit the same density and nearly the same crystalline form as those of the components; the possession of these characteristics is traced to the existence of the separate optically active compounds twinned together, either microscopically or macroscopically, in the pseudoracemic crystals.

Whilst pseudoracemic substances necessarily exhibit a close similarity in crystal form to the component compounds, very few instances are known in which a distinct morphotropic relationship has been shown to exist between a truly racemic substance and its optically active components. The most striking case of such a relationship is probably afforded by sobrerol; Armstrong and Pope showed (Trans., 1891, **59**, 315) that *d*- and *l*-sobrerol belong to the hemimorphous monosymmetric class with

$$a:b:c=2{\cdot}4113:1:0{\cdot}8531,\ \beta=83^\circ 38',$$

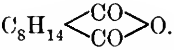
whilst the racemic compound is orthorhombic with

$$a:b:c=2{\cdot}4242:1:0{\cdot}8268.$$

Although the two substances crystallise in totally different systems and classes, a very close dimensional relationship obviously holds between them (Pope, Trans., 1896, **69**, 977).

The work of Barlow and Pope on the relation between crystalline form and chemical constitution (Trans., 1906, **89**, 1675; 1907, **91**, 1150; 1908, **98**, 1528; 1910, **97**, 2308), and especially that part of it which relates to polymorphism, indicates that a close morphotropic relationship should exist between truly racemic compounds and their optically active components; as it is now evident that the work of these authors provides a secure working hypothesis (Jerusalem, Trans., 1909, **95**, 1275; 1910, **97**, 2190), and elucidates clearly the relation between constitution and crystal form, I have studied a number of optically active substances and the corresponding racemic compounds. As a result of this work it has been found that the anticipated morphotropic relationship exists in a considerable number of cases.

Racemic Camphoric Anhydride,



$$C_8H_{14}{<}\substack{CO\\CO}{>}O.$$

l-Camphoric acid, prepared by Noyes' (*Amer. Chem. J.*, 1894, **16**, 500) method, was crystallised from alcohol with an equal quantity of *d*-camphoric acid; the externally compensated camphoric acid thus obtained was converted into the anhydride and the imide as described by Noyes. The *dl*-camphoric acid could only be obtained in minute needles unsuitable for crystal measurement. *dl*-Camphoric anhydride separates from alcohol and ethyl acetate in well-defined transparent prisms.

Crystalline System.—Monosymmetric:

$$a:b:c = 0{\cdot}5493:1:0{\cdot}2799;\ \beta = 91^\circ 38' 20''.$$

Forms observed: $a\{100\}$, $b\{010\}$, $p\{110\}$, $m\{10\bar{1}\}$, $o\{121\}$. The form $\{010\}$ is dominant, $a\{100\}$, $p\{110\}$, and $m\{10\bar{1}\}$ are about equally largely developed, whilst $o\{121\}$ is small and not always present. No distinct cleavage plane was observed.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
110 : 010	22	60°46′—61°35′	61°13′30″	—
$10\bar{1}$: 110	17	67 26 —67 50	67 40 20	—
010 : 121	14	63 25 —64 2	63 45 30	—
100 : $10\bar{1}$	16	64 2 —64 34	64 13 50	64°18′50″
$10\bar{1}$: $\bar{1}2\bar{1}$	5	57 58 —58 28	58 3 40	58 10 30
100 : 110	6	28 38 —28 53	28 47 20	28 46 30
121 : 110	5	54 7 —54 30	54 14 0	54 9 10
121 : $1\bar{2}1$	4	52 12 —52 47	52 26 0	52 29 0

In order to compare this crystalline form with those of *d*-camphoric anhydride and the additive compound of *d*-camphoric acid with acetone, $2C_{10}H_{16}O_4,(CH_3)_2CO$, measured by Pope (Trans., 1896, **69**, 1696), it is conveniently referred to a new set of axes, namely,

$$a':b':c' = a:c:b/2 = 1{\cdot}9622:1:1{\cdot}7860;\ \gamma = 91^\circ 38' 20''.$$

This change is justified by the occurrence of the form $o\{121\}$, and the axial ratios thus transformed give the equivalence parameters:

$$x:y:z=5{\cdot}0576:2{\cdot}5775:4{\cdot}6034;\ \gamma=91^\circ 38' 20''.\quad W=60.$$

d-Camphoric anhydride is orthorhombic with

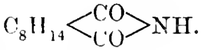
$$a:b:c=0{\cdot}9989:1:1{\cdot}7251;$$

on multiplying the ratio a/b by two, which is justified by the occurrence of the forms $\{102\}$ and $\{120\}$, the axial ratios and equivalence parameters are obtained as:

$$a':b':c'=2a:b:c=1{\cdot}9980:1:1{\cdot}7251, \text{ and}$$
$$x:y:z=5{\cdot}1782:2{\cdot}5917:4{\cdot}4709;\ W=60.$$

The axial ratios and the equivalence parameters of the two substances respectively exhibit a close agreement. A few measurements of *dl*-camphoric anhydride have been given by Kraatz, but, as Groth has indicated ("Chemische Krystallographie," 1910, Vol. III., 732), the values are vitiated by some error.

d-*Camphorimide*,



$C_8H_{14}<\begin{smallmatrix}CO\\CO\end{smallmatrix}>NH$.

This substance separates from its alcoholic solution in small, colourless, transparent prisms.

Crystalline System.—Monosymmetric: $a:b:c=1{\cdot}0051:1:0{\cdot}7297$; $\beta=92^\circ 5' 10''$.

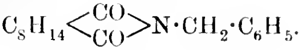
Forms observed: $a\{100\}$, $p\{110\}$, $r\{101\}$, $s\{10\bar{1}\}$, and $o\{12\bar{1}\}$. The form $\{100\}$ is dominant, and $\{110\}$ is in general very small. No distinct cleavage was observed.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$100:10\bar{1}$	15	55° 4′—55°54′	55°23′30″	—
$10\bar{1}:12\bar{1}$	22	49 56 —50 30	50 13 20	—
$100:110$	28	44 56 —45 26	45 7 40	—
$100:101$	14	52 36 —53 3	52 48 40	52°39′30″
$100:12\bar{1}$	9	68 33 —68 58	68 42 20	68 41 30
$110:121$	8	72 55 —73 29	73 17 0	73 14 40
$110:12\bar{1}$	7	36 38 —36 56	36 48 10	36 47 10
$121:12\bar{1}$	9	79 24 —79 53	79 38 0	79 33 20

dl-Camphorimide crystallises from alcohol in small prisms, which goniometrically could not be distinguished from the crystals of the *d*-imide; no comparison is necessary between these two substances, and the former is probably pseudoracemic.

After dividing unit length along the axis-b by two, the axial ratios and equivalence parameters are obtained in the form:

$$a':b':c'=a:b/2:c=2{\cdot}0102:1:1{\cdot}5594;\ \beta=92^\circ 5' 10'',$$
$$x:y:z=5{\cdot}5590:2{\cdot}7654:4{\cdot}0358;\ \beta=92^\circ 5' 10''.\quad W=62.$$



d-*Camphorbenzylimide*, $C_8H_{14}<\substack{CO\\CO}>N\cdot CH_2\cdot C_6H_5$.

d-Camphorbenzylimide was prepared in this laboratory by Evans (Trans., 1910, **97**, 2240), and the crystals were measured for comparison with those of the parent imide and its *p*-nitrobenzyl derivative; it separates from ethyl acetate solution in small, colourless prisms.

Crystalline System.—Tetragonal: $a:c=1:2\cdot3207$.

Forms observed: $c\{001\}$, $p\{101\}$, and $o\{221\}$. The faces of the form $p\{101\}$ are the largest, those of $c\{001\}$ smaller, and $o\{221\}$ is entirely subordinate. A perfect cleavage is to be observed parallel to the faces of $p\{101\}$.

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
001 : 101	35	66°33′—66°52′	66°41′20″	—
101 : $10\bar{1}$	17	46 29 —46 46	46 38 10	46°37′10″
101 : $01\bar{1}$	17	80 49 —81 14	80 58 50	80 59 30
221 : $22\bar{1}$	3	33 50 —33 54	33 51 40	33 53 20
001 : 221	2	73 5 —73 5	73 5 0	73 5 20
101 : 221	20	42 22 —42 46	42 32 50	42 33 50

The equivalence parameters are conveniently calculated after referring the goniometric dimensions to an orthorhombic axial system, such that the new axial ratios:

$$a':b':c'=c:a:2a=2\cdot3207:1:2.$$
$$x:y:z=6\cdot3923:2\cdot7545:5\cdot5090.\quad W=96.$$

On comparing these values with those obtained for *d*-camphorimide, namely, $x:y:z=5\cdot5590:2\cdot7654:4\cdot0358$, it is seen that y, which has approximately the z-value for benzene, 2·780 (Barlow and Pope, Trans., 1906, **89**, 1695), remains practically unchanged, and that the whole weight of the increase in valency volume is borne by the equivalence parameters x and z.

d-*Camphor*-p-*nitrobenzylimide*, $C_8H_{14}<\substack{CO\\CO}>N\cdot CH_2\cdot C_6H_4\cdot NO_2$.

This substance was also prepared by Evans (*loc. cit.*), and is deposited from alcoholic solution in small, massive, colourless prisms.

Crystal System.—Monosymmetric, hemimorphous class:

$$a:b:c=5\cdot0148:1:3\cdot5525;\ \beta=95°26'20''.$$

Forms observed: $a\{100\}$, $p\{101\}$, $q\{10\bar{1}\}$, $o\{111\}$, and $w\{31\bar{1}\}$. The forms $\{100\}$, $\{101\}$, $\{10\bar{1}\}$, and $\{311\}$ are equally well developed; $\{111\}$ is small and invariably represented by but two planes, those on one side of the monosymmetric plane of symmetry.

The crystal structure is thus that of the hemimorphous class of the monosymmetric system.

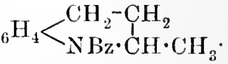
Angle	Number of measurements.	Limits.	Mean.	Calculated.
$100 : 10\bar{1}$	25	58°12′—58°32′	58°21′10″	—
$10\bar{1} : 31\bar{1}$	30	60 44 —61 15	61 4 20	—
$100 : 31\bar{1}$	29	62 37 —63 17	62 53 20	—
$101 : 111$	12	69 53 —70 12	70 4 30	70° 7′ 0″
$111 : \bar{1}1\bar{1}$	5	39 44 —39 49	39 47 50	39 46 0
$100 : 111$	11	77 35 —77 44	77 37 20	77 40 10
$111 : \bar{3}11$	12	41 8 —41 24	41 14 10	41 15 30
$111 : \bar{1}01$	11	83 14 —83 33	83 23 30	83 29 40
$\bar{3}11 : 31\bar{1}$	16	65 6 —65 24	65 14 50	65 11 14

The equivalence parameters are calculated after multiplying the length of the axis-*b* by two, so that:

$$a' : b' : c' = a : b/2 : c = 2{\cdot}5074 : 1 : 1{\cdot}7762.$$
$$x : y : z = 7{\cdot}1546 : 2{\cdot}8553 : 5{\cdot}0682 ;\ \beta = 95^\circ 26' 20''. \quad W = 102.$$

On comparing these values with those for *d*-camphorimide and for *d*-camphorbenzylimide, it will be observed that the greatest increase occurs in the *x*-parameter, whilst that of *y* had remained almost unchanged.

A study of the goniometric data which are already available for a number of racemic and optically active isomerides indicates that morphotropic relationships similar to those above shown to exist between the racemic and optically active forms of camphoric anhydride may be readily traced in almost all cases; several of these will now be considered.

The *d*- and *l*-benzoyltetrahydroquinaldines,  $C_6H_4{<}\begin{matrix}CH_2-CH_2\\ NBz\cdot CH\cdot CH_3\end{matrix}$ were described and crystallographically examined by Pope and Peachey (Trans., 1899, **75**, 1075); they are monosymmetric with the axial ratios:

$$a : b : c = 1{\cdot}0277 : 1 : 0{\cdot}4261 ;\ \beta = 91^\circ 45'.$$

The equivalence parameters may be calculated after multiplying the ratio, c/b, by two, so that:

$$a' : b' : c' = a : b : 2c = 1{\cdot}0277 : 1 : 0{\cdot}8522 ;\ \beta = 91^\circ 45'.$$
$$x : y : z = 4{\cdot}8144 : 4{\cdot}6847 : 3{\cdot}9923 ;\ \beta = 91^\circ 45'. \quad W = 90.$$

The corresponding racemic compound was assigned to the monosymmetric system by the same observers (*loc. cit.*, p. 1091) with the axial ratios:

$$a : b : c = 0{\cdot}6768 : 1 : 0{\cdot}6675 ;\ \beta = 98^\circ 56'.$$

The planes (101), $(\bar{1}01)$, (001), (110), and (111) may be equally well described as (001), (100), (101), $(\bar{1}11)$, and (210) respectively;

when the transposition thus indicated is made, the axial ratios and equivalence parameters become:

$$a:b:c=1{\cdot}0218:1:0{\cdot}8739;\ \beta=90^\circ 48'.$$

$$x:y:z=4{\cdot}7554:4{\cdot}6540:4{\cdot}0699;\ \beta=90^\circ 48'.\quad W=90.$$

The agreement between the axial ratios and the equivalence parameters of the optically active substances on the one hand, and the racemic compound on the other, is now seen to be exceedingly close, as close, in fact, as is observable between the same constants for members of an isomorphous series.

The *d*- and *l*-camphoroximes were found by Muthmann (*Zeitsch. Kryst. Min.*, 1889, **15**, 402) to be monosymmetric with the axial ratios:

$$a:b:c=1{\cdot}0252:1:0{\cdot}6073;\ \beta=99^\circ 42'.$$

The racemic compound formed by the two isomerides was found by Pope (Trans., 1897, **71**, 1048) also to be monosymmetric with the axial ratios:

$$a:b:c=1{\cdot}2579:1:0{\cdot}7723;\ \beta=124^\circ 12'.$$

On so transposing this set of axial ratios that the planes (100), (110), $(10\bar{1})$, $(11\bar{1})$, and (001) assume the indices (100), (110), (001), (011), and $(10\bar{1})$ respectively, the axial and equivalence parameters become:

$$a:b:c=1{\cdot}0424:1:0{\cdot}7723;\ \beta=93^\circ 35' 20''.$$

$$x:y:z=4{\cdot}4379:4{\cdot}2574:3{\cdot}2880;\ \beta=93^\circ 35' 20''.\quad W=62.$$

The agreement between the equivalence parameters for the optically active substances and the truly racemic compound is again quite good.

A close, but hitherto unrecorded, relationship exists between the crystalline forms of the hydrogen tartrates and the hydrogen racemates of the alkali metals; the data quoted below are given in Groth's "Chemische Krystallographie" (1910, Vol. III) by the authors, and at the pages, stated. The anhydrous hydrogen tartrates are orthorhombic, and for the purposes of the comparison it is convenient to transpose the axial ratios, so that:

$$a':b':c'=b:c:a.$$

Hydrogen tartrate of	$a : b : c$.	$a' : b' : c'$.	Author.	Page.
Potassium	0·7116 : 1 : 0·7292	1·3713 : 1 : 0·9759	Gossner	318
Rubidium	0·6972 : 1 : 0·7228	1·3835 : 1 : 0·9646	,,	320
Cæsium	0·6610 : 1 : 0·6937	1·4415 : 1 : 0·6937	Cooke	320
Ammonium ...	0·6950 : 1 : 0·7172	1·3942 : 1 : 0·9691	Gossner	321

The hydrogen racemates of the alkali metals also crystallise without water, and are monosymmetric; it is convenient to transpose the data originally given so that the planes (001), (101), $(\bar{1}01)$, (011), and $(11\bar{2})$ become (100), $(20\bar{1})$, (001), (210), and (212) respectively. The original axial ratios are first given below, and are followed by the values transposed as described.

Hydrogen racemate of	$a:b:c$ original.	$a:b:c$ transposed.	Author.	Page.
Potassium	0·9771 : 1 : 1·5476 $\beta=116°18'$	1·4168 : 1 : 0·9768 $\beta=101°52'$	Schacchi	361
Rubidium	0·9569 : 1 : 1·4777 $\beta=114°38'$	1·3834 : 1 : 0·9518 $\beta=103°50'$	Wyrouboff	362
Ammonium ...	0·9823 : 1 : 1·5955 $\beta=114°33'$	1·4858 : 1 : 0·9815 $\beta=102°21'$	Schacchi	363

From the axial ratios last given for the hydrogen tartrates and hydrogen racemates respectively, the equivalence parameters are calculated as follows:

Metal.	Hydrogen tartrate $a:b:c$	Hydrogen racemate. $a:b:c$	W.
Potassium	4·0315 : 2·9398 : 2·8688 $\beta=90°$	4·1478 : 2·9285 : 2·8605 $\beta=101°52'$	34
Rubidium	4·0710 : 2·9425 : 2·8383 $\beta=90°$	4·1291 : 2·9849 : 2·8410 $\beta=103°50'$	34
Cæsium	4·2011 : 2·9143 : 2·7770 $\beta=90°$	—	34
Ammonium	4·3133 : 3·0935 : 2·9978 $\beta=90°$	4·5159 : 3·0394 : 2·9833 $\beta=102°21'$	40

The close correspondence between the equivalence parameters for the corresponding hydrogen tartrates and racemates, calculated after the described transpositions have been performed, is of the same order as that observed between members of the same isomorphous series.

Several of the normal tartrates of the alkali metals are hexagonal, and hence seem to possess crystal structures derived from another close-packed arrangement than are the hydrogen tartrates; ammonium and thallium tartrate are, however, closely related morphotropically to the foregoing.

Ammonium tartrate is monosymmetric with the axial ratios: $a:b:c=1·1506:1:1·4383$; $\beta=92°23'$ (Gossner, *loc. cit.*, p. 325); on transposing the axes a and c and calculating the equivalence parameters, values are obtained which are closely related to those given above for ammonium hydrogen tartrate:

	$x:y:z$	β.	W.
$NH_4HC_4H_4O_6$.....................	4·3133 : 3·0935 : 2·9978	90°	40
$(NH_4)_2C_4H_4O_6$	4·3582 : 3·0301 : 3·4864	92°23′	46

The effect of introducing the second ammonium radicle is to leave the type of crystal structure unaltered, inasmuch as the values x and y are almost the same for the two substances, and the main weight of the increase of valency volume is borne by the value z.

Thallium tartrate is dimorphous, one modification being hexagonal and isomorphous with potassium tartrate, whilst the other is monosymmetric with the axial ratios: $a:b:c = 1{\cdot}1878:1:0{\cdot}6814$; $\beta = 93^\circ 17'$ (Wyrouboff, Groth's "Chemische Krystallographie," 1910, Vol. III., 327). The equivalence parameters given below are calculated after interchanging a and c, and afterwards multiplying the new value of a by two. Thallium racemate crystallises in two monosymmetric modifications, the second of which has the axial ratios $a:b:c = 1{\cdot}1860:1:1{\cdot}2955$; $\beta = 96^\circ 45'$ (Des Cloizeaux, Groth's "Chemische Krystallographie," 1910, Vol. III., 367); the equivalence parameters are calculated after interchanging the values a/b and c/b:

	$x : y : z$.	β.	W.
Thallium tartrate	3·7622 : 2·7606 : 3·2791	90°	34
Thallium racemate	3·6456 : 2·8140 : 3·3374	96°45′	34

It is evident that in this case also a very close morphotropic relationship exists between the salts of the optically active and the racemic acid.

From the results of the above investigation the conclusion is to be drawn that a close morphotropic relationship exists between the crystalline forms of corresponding salts of optically active and racemic acids, and that this relationship is precisely of the kind foretold by the theory of Barlow and Pope concerning the connexion of crystalline form with chemical composition and constitution.

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CXXXVIII.—*The Velocity of the Hydrogen Ion, and a General Dissociation Formula for Acids.*

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WHILST the mobilities of most of the common ions have been definitely determined to an accuracy of one-tenth of a unit, the value for the velocity of the hydrogen ion, which is the most important from theoretical considerations, is not known more exactly than within several units. The experimental difficulties in the two methods available for the determination of ionic velocities are here much greater than is the case with other ions. In conductivity measurements the impurities contained in the water used have prevented the accurate determination of the equivalent conductivities of acids at very high dilutions, and no trustworthy correction for the influence of these impurities has yet been applied, as has been done for salts. The values obtained from the measurement of migration ratios are also less accurate, since the preponderating mobility of the hydrogen ion causes a small error in the ratio obtained to exert a comparatively large influence on the ionic velocity deduced from it. The results from both methods have proved very conflicting, as the following figures, which are the results of the chief researches on the mobility of the hydrogen ion, will serve to show. All values are expressed in terms of the reciprocal ohm.

Ostwald, from conductivity measurements with hydrochloric acid, obtained the value 342 at 25° (*Zeitsch. physikal. Chem.*, 1888, **2**, 842), and employed this figure in the calculation of the dissociation constants of all the weak acids subsequently examined (*Zeitsch. physikal. Chem.*, 1889, **3**, 172). The value was afterwards raised to 347 ("Lehrbuch der Allgemeinen Chemie," 1893, **2**, 675).

Kohlrausch ("Leitvermögen der Electrolyte," 1898, pp. 107–10, 200) deduced, by the application of an empirical formula to the results of conductivity measurements with dilute solutions of hydrochloric and nitric acids, the provisional value of 318 at 18°, or 352 at 25°. Until recently the above values of Ostwald and Kohlrausch have been adopted for the calculation of dissociation ratios.

The measurement of migration ratios was not of sufficient accuracy to be used for the purpose of determining the velocity of the hydrogen ion until an improved apparatus was devised by Noyes (*Zeitsch. physikal. Chem.*, 1901, **36**, 69). With this, a determination of the mobility by the method of migration ratios was attempted by Noyes and Sammet (*Zeitsch. physikal. Chem.*, 1903, **43**, 49), hydrochloric acid being used as the electrolyte. The unexpectedly high value of 365 was obtained.

It has been shown by Rothmund and Drucker (*Zeitsch. physikal. Chem.*, 1903, **46**, 827), in the course of an investigation on the dissociation of picric acid, that lower values for the velocity of the hydrogen ion give results for the degree of dissociation which are more satisfactory than those obtained with the use of Kohlrausch's figure, 352. A value as low as 338 is suggested, and tested with several strong acids. The subject is further developed by Drucker in a later paper (*Zeitsch. physikal. Chem.*, 1904, **49**, 563), where it is demonstrated that $H^{\cdot} = 312$ at 18° (that is, 345 at 25°) gives more satisfactory values for the dissociation constants of weak acids than does the higher figure of Kohlrausch.

The results of the investigations of several observers, both on conductivities and on migration ratios, are collected and compared by Drucker in a third paper (*Zeitsch. Elektrochem.*, 1907, **13**, 81). The measurements of the equivalent conductivities of dilute solutions of hydrochloric and nitric acids by Goodwin and Haskell (*Proc. Amer. Acad.*, 1904, **40**, 399), and of sulphuric acid by Whetham (*Zeitsch. physikal. Chem.*, 1906, **55**, 200), are combined with the migration ratios obtained with the same acids by Jahn and his pupils (*Zeitsch. physikal. Chem.*, 1901, **37**, 707) and Tower (*J. Amer. Chem. Soc.*, 1904, **26**, 1039) respectively. The mean value deduced for the velocity of the hydrogen ion is 313 at 18°, or 346 at 25°. From the results obtained it is inferred that the figure given by Kohlrausch is certainly too high.

Kohlrausch (*Zeitsch. Elektrochem.*, 1907, **13**, 333), whilst admitting that his former value was claimed to be merely an approximation, takes also into account further migration ratios recently determined by Jahn and his pupils (*Zeitsch. physikal. Chem.*, 1907, **58**, 641), and puts forward as the most probable value for the velocity of the hydrogen ion the figure 315 at 18°, or 348 at 25°.

Gorke (*Zeitsch. physikal. Chem.*, 1908, **61**, 495) obtained, by the measurement of the equivalent conductivities of dilute solutions of picric acid, the value 353 at 25°.

Noyes and Kato (*Zeitsch. physikal. Chem.*, 1908, **62**, 420), from the migration ratios obtained with dilute solutions of nitric and hydrochloric acids, were led to the conclusion that the velocity of the hydrogen ion varies considerably with the concentration. For solutions under one-thousandth normal its value may be taken as 315 at 18° (that is, 348 at 25°); for more concentrated solutions it is several per cent. higher. This theory of a change of mobility with the concentration had been previously advanced by Jahn (*Zeitsch. physikal. Chem.*, 1900, **33**, 545; **35**, 8) as applying to the ions of all strong electrolytes, and affording an explanation of the breakdown of the dilution law of Ostwald. The assumption of a varying mobility in dilute solution has, however, been vigorously criticised on many sides, and may be regarded as not yet confirmed (Wegscheider, *Zeitsch. physikal. Chem.*, 1909, **69**, 503).

From migration ratios obtained with dilute solutions of hydrochloric acid, Drucker and Kršnjavi (*Zeitsch. physikal. Chem.*, 1908, **62**, 731) have concluded that 313 at 18° (that is, 346 at 25°) is the maximum possible value for the velocity of the hydrogen ion.

In the above summary of investigations it will be seen that the values obtained range from a minimum of 338 to a maximum of 365; the general results of the more recent experiments are, however, within the much narrower limits of 345 to 348. The value must be determined more definitely than this before the problem regarding the dissociation of strong acids can be solved by the substantiation of any formula from the figures of experiment.

The failure to obtain satisfactory conductivity measurements with very dilute solutions of strong acids has been attributed to the influence of the impurities in the water used, namely, carbonic acid and ammonia from the atmosphere, and alkali from the glass vessels employed. No satisfactory correction can be applied, since the mutual influence of the substances in solution on their dissociation is quite uncertain (Kohlrausch, "Leitvermögen der Electrolyte," 1898, p. 92). The figures are, in general, given without any correction, and the degree of error is unknown. Any deductions from the results cannot, therefore, unless supported by other evidence, be regarded as conclusive; thus Kohlrausch (*Zeitsch. Elektrochem.*, 1907, **13**, 646) states, after a criticism of conclusions drawn by Bogdan from experiments with dilute solutions of hydrochloric and nitric acids (*Zeitsch. Elektrochem.*, 1907, **13**, 596): "The last word upon the subject of dilute acids and bases will certainly not be spoken until we have succeeded in investigating the solutions in pure water."

The water used in the following conductivity experiments was obtained by distillation, in the open air, from water to which a little Nessler's solution has been added. Jena-glass flasks and a bent tube of pure tin, fitted with a condenser, were used, and spirting-over was prevented by a series of constrictions in the upright portion of the tube. The first distillation gave water with a specific conductivity of $1{\cdot}20 \times 10^{-6}$ at 25°; by a second distillation this was reduced to $0{\cdot}90 \times 10^{-6}$. This value did not increase appreciably on exposure to outside air. Water of specific conductivity $0{\cdot}70 \times 10^{-6}$ was obtained by distillation in silica vessels, but on transference to a glass cell the value quickly rose to $0{\cdot}90 \times 10^{-6}$ at 25°.

With the water available for use in conductivity measurements possessing a specific conductivity of at least $0{\cdot}90 \times 10^{-6}$ at 25°, it did not seem probable that the results obtained from dilute acid solutions could be of sufficient accuracy to prove of service in the determination of the velocity of the hydrogen ion. Nevertheless, it was found possible, by a modification of the method for determining the value of the equivalent conductivity at infinite dilution, to obtain with acids of a certain strength very satisfactory results.

It has been observed previously by Drucker (*Zeitsch. physikal. Chem.*, 1904, **49**, 563) that the dissociation constants obtained for weak acids are more or less satisfactory according to the value for the velocity of the hydrogen ion that is employed in the calculation of the equivalent conductivity at infinite dilution. The fact that lower values than Kohlrausch's figure of 352 give more satisfactory dissociation constants for weak acids than does the latter, was considered by Drucker as a strong argument for the assumption that the value of Kohlrausch was too high. The point, however, seems to have escaped observation that with acids of a certain strength a satisfactory dissociation constant at high dilutions is to be obtained with the use of one particular value for the velocity of the hydrogen ion, and not with the use of any other value.

As an illustration of this point, the results obtained from one series of conductivity measurements of cyanoacetic acid at 25° are given below in table I. The method of experiment is described in full subsequently; the water employed possessed a specific conductivity of $0{\cdot}90 \times 10^{-6}$ at 25°.

The first column gives the dilution v, the second the equivalent conductivity μ. The dissociation constants $100k_1$ and $100k_2$ are calculated with the use of the values of Ostwald and of Kohlrausch, $\mathrm{H}^{\cdot}=347{\cdot}0$ and $\mathrm{H}^{\cdot}=352{\cdot}0$ respectively. In the third column the percentage dissociation, using the value $\mathrm{H}^{\cdot}=347{\cdot}0$, is shown. The mobility of the anion is taken as 38·9 (see table IX below).

TABLE I.

Cyanoacetic Acid. Water, $0{\cdot}9 \times 10^{-6}$.

v.	μ.	100 m.	100 k_1 ($\mathrm{H}^{\cdot}=347{\cdot}0$).	100 k_2 ($\mathrm{H}^{\cdot}=352{\cdot}0$).
20·80	96·2	24·93	0·398	0·386
41·60	127·1	32·93	0·389	0·376
83·20	164·5	42·63	0·381	0·368
166·4	207·3	53·71	0·375	0·360
332·8	252·4	65·40	0·372	0·354
665·6	294·9	76·40	0·372	0·348
1331·0	329·2	85·32	0·372	0·338
2662·0	353·2	91·52	0·371	0·318
5324·0	368·3	95·44	0·375	0·288

For the above series it is evident that the value $\mathrm{H}^{\cdot}=347{\cdot}0$ gives a far more satisfactory constant than the value $\mathrm{H}^{\cdot}=352{\cdot}0$. Indeed, a satisfactory dissociation constant for the dilute solutions of the series can be obtained only within a very limited region about $\mathrm{H}^{\cdot}=347{\cdot}0$. Values only a few tenths of a unit removed from this produce appreciable divergences in the constant.

With acids of this type it is possible, therefore, after the measurement of a number of conductivity series, carried to high dilutions, to obtain from each series that value for the velocity of the hydrogen ion that is required to give a satisfactory dissociation constant, and, by comparison of the values obtained, to ascertain to what degree of accuracy the determination can be carried. This has been done in the experiments described below.

The acids that can be employed are of a very limited range of strength, namely, those which possess a dissociation constant between the limits of 0·001 and 0·01. Acids of this type pass from slight to almost complete dissociation within the ordinary range of dilutions. With acids possessing a smaller dissociation constant, the constant obtained is fairly satisfactory through a large variation in the value taken for the velocity of the hydrogen ion, and no definite value for the latter can be deduced. With stronger acids, dissociation is so nearly complete in dilute solution that the errors of experiment exert sufficient influence, since they are greatly magnified in the calculation of the dissociation constant, to prevent any value taken giving a satisfactory constant. In the more concentrated solutions of these stronger acids, where the degree of dissociation is not so great, the dilution law of Ostwald is not exactly obeyed, as will be shown later.

The above difficulties exist even within the narrow limits indicated, and acids possessing dissociation constants near the centre of the range were found to be far more useful than those having constants near the upper or lower limit. Suitable acids are, however, very few in number. Acids of as simple a constitution as possible must be chosen, in order to avoid the presence of any group likely to cause complications at high dilutions. The acids employed were all, in fact, simple substituted acetic and benzoic acids:

Cyanoacetic acid	$k=0·00368$
o-Nitrobenzoic acid	$k=0·00620$
o-Chlorobenzoic acid	$k=0·00128$
3 : 5-Dinitrobenzoic acid	$k=0·00157$

Of these, cyanoacetic acid was the most suitable. *o*-Nitrobenzoic acid, owing to its larger dissociation constant, gives results which are appreciably affected by the errors of experiment, whilst the remaining acids, which possess smaller constants, give results from which the value deduced is rather indeterminate.

It is obviously essential that the acids should be quite pure; they were therefore repeatedly crystallised until constant conductivity values at high dilutions were obtained. *o*-Chlorobenzoic and 3:5-dinitrobenzoic acids were specially prepared.

o-Chlorobenzoic acid was prepared by the distillation of salicylic acid with phosphorus pentachloride, as described by Hübner (*Annalen*, 1884, **222**, 192). The mixed chlorides obtained were decomposed by water, and steam was passed through the solution for several hours until all salicylic acid was removed. *o*-Chlorobenzoic acid was then obtained pure by recrystallisation from water.

3:5-Dinitrobenzoic acid was prepared by the nitration of benzoic acid, as described by Shukoff (*Ber.*, 1895, **28**, 1800), and purified by several crystallisations from water.

Cyanoacetic acid, being extremely soluble in water, was recrystallised from benzene until pure. Owing to the deliquescent nature of the acid, all solutions were made up volumetrically. *o*-Nitrobenzoic acid was obtained pure by repeated crystallisations from water.

The conductivity measurements were carried out with the greatest possible accuracy. The cells used were of the type described by Cantor (*Zeitsch. Elektrochem.*, 1903, **9**, 922). The cell constants were determined by means of *N*/50- and *N*/100-potassium chloride (Kahlbaum's 100·00 per cent.). With solutions made up independently, values were obtained all agreeing within 1 in 2000.

The dilutions were carried out in the cell itself by means of 30 c.c. and 60 c.c. graduations. The accuracy of these was tested by weighing the water run out at a known temperature. Correct volumes of 30 c.c. are not necessary; all that is required for accurate dilution is that the two volumes shall be equal. The correct graduations for doubling the volume were determined for each cell within an error of 0·01 c.c. in 30 c.c.

The conductivities of the solutions were measured by means of a rotating commutator and a galvanometer. By this method the results obtained at high dilutions are much more accurate than with the usual induction coil and telephone. The bridge employed was a three-metre platinum wire, divided into one thousand parts; readings could easily be obtained within one-tenth of a division, the galvanometer being used as a zero instrument, at all dilutions.

The cells were immersed in a small thermostat, heated beneath, and regulated to 25°. The copper sides of the bath were not protected in any way, and convection was sufficient, without any stirring at all, to keep the temperature constant. The cells were suspended away from the sides, and the temperature in their neighbourhood was never found to vary more than 0·03° from 25°.

The acid solutions used were standardised either volumetrically or gravimetrically. In the former case a known volume was titrated with barium hydroxide solution, phenolphthalein (except where otherwise stated) being used as indicator. The barium hydroxide solution (approximately *N*/100) was standardised against *N*/10-hydrochloric acid, and also against certain of the acids used—the results obtained were in agreement within 1 in 1000.

In the latter case a weighed quantity of acid was dissolved in water and made up to a known volume. All weights were reduced, with sufficient accuracy, to true weights in vacuum by addition of one-thousandth part. This is the correction for substances with a specific gravity slightly greater than unity, and is accurate for the acids used well within the limits of error in weighing. All volumes were reduced to volumes occupied at 25°.

The results obtained by the above methods were, on comparison, usually in agreement within 1 in 1000; the greatest divergence was 1 in 600. This may be taken as the maximum degree of error in the estimation of the concentration of a solution.

The graduation of the cells is accurate within 0·01 c.c. of 30 c.c., as described above; the various dilutions in a conductivity series were not carried out, however, within a greater accuracy than 0·03 c.c. in 30 c.c. This is due to considerations of time, since for more exact dilutions it is necessary to allow the cell to remain for a long period, in order to drain completely, before each reading. A series must be completed as quickly as possible, and with the above apparatus the measurements are already protracted, since the large glass surface of the cell is slow in attaining the true temperature of the thermostat, from which the cell must be removed during the mixing of the solutions. Greater accuracy than the above (1 in 1000) was therefore not aimed at in the dilutions. The error is not so important as may at first sight appear, since it is not (as is the initial error in the graduation) doubled at each step, but is equally likely to be positive or negative at each dilution. Indeed, as has often been pointed out, the most important error incurred in conductivity determinations is in the estimation of the initial concentration of a solution. Two series, differing slightly in their first values, will usually run parallel throughout their whole length.

There remains the question of the influence of the impurities in the water on the values of the equivalent conductivity obtained for very dilute solutions. In the series for cyanoacetic acid given above, no correction has been made for this. From the figures obtained it seems that the impurities in the water used do not affect the value appreciably until a high dilution is reached. Here a small increase is observable, still, however, within the limits of experimental error. A small difference in the value taken for the velocity of the hydrogen ion produces a much greater effect on the dissociation constant; the influence of the water impurities cannot therefore be directly measured.

We can determine, however, to what dilutions the experiments can be carried without taking the influence of the water into account, by examination of the results obtained with dilute solutions of a much weaker acid. In such solutions any small error in the value taken for the velocity of the hydrogen ion does not influence the dissociation constant, owing to the less complete dissociation;

at the same time the specific conductivity of the solutions is small, and the influence of the water on the value obtained is more readily perceived.

With this object preliminary experiments were carried out with acetic acid. Two series of conductivity measurements were performed; the water used for dilution possessed a specific conductivity of $0·90 \times 10^{-6}$ in the first series, and of $1·20 \times 10^{-6}$ in the second. The results obtained are given in tables II and III; the value of the equivalent conductivity at infinite dilution is taken as 387·7 ($H^{\cdot} = 347·0$; $Ac' = 40·7$) (Bredig, *Zeitsch. physikal. Chem.*, 1894, **13**, 218).

TABLE II.

Acetic Acid. Water, $0·90 \times 10^{-6}$.

v.	μ.	100m.	100k.
13·57	6·086	1·570	0·001845
27·14	8·591	2·216	0·001851
54·28	12·09	3·118	0·001849
108·56	16·98	4·380	0·001849
217·1	23·81	6·141	0·001851
434·2	33·22	8·568	0·001849
868·4	46·13	11·90	0·001850
1737·0	63·60	16·41	0·001854
3474·0	86·71	22·36	0·001855
6948·0	116·8	30·13	0·001870
∞	387·7	—	—

TABLE III.

Acetic Acid. Water, $1·20 \times 10^{-6}$.

v.	μ.	100m.	100k.
15·816	6·561	1·692	0·001842
31·63	9·260	2·388	0·001848
63·26	13·03	3·361	0·001847
126·52	18·30	4·721	0·001848
253·04	25·60	6·603	0·001846
506·1	35·67	9·200	0·001843
1012·2	49·50	12·77	0·001846
2024·4	68·22	17·60	0·001856
4049·0	93·5	24·12	0·001893
8098·0	125·8	32·45	0·001924
∞	387·7	—	—

In the first series a very satisfactory dissociation constant is obtained, without the application of any correction, up to $v = 3500$; with water of a slightly higher specific conductivity, in the second table, the constant has already begun to show an increase at $v = 2000$.

It seems reasonable to suppose, therefore, that with the use of water of a specific conductivity $0·90 \times 10^{-6}$ at 25°, the measurements with stronger acids can be relied on, without any correction, up to high dilutions, as in table I. To test this further, however, and to find by experiment what effect the specific conductivity of the water used has on the value for the velocity of the hydrogen ion deduced from the measurements with these acids, the following plan was adopted. A conductivity series of each acid was carried out with four different samples of water, possessing the following specific conductivities at 25°:

$$(a)\ 0{\cdot}90 \times 10^{-6};\ (b)\ 1{\cdot}20 \times 10^{-6};\ (c)\ 1{\cdot}80 \times 10^{-6};\ (d)\ 2{\cdot}50 \times 10^{-6}.$$

The first two samples were obtained as described above; (*c*) is an earlier fraction of the first distillation; (*d*) is the ordinary distilled water of the laboratory.

The conductivity results obtained are expressed in tables V to XII. It is necessary, however, first of all to determine the equivalent conductivities of dilute solutions of the sodium salts of the acids employed, in order to obtain accurate values for the velocities of their respective anions.

The measurement of these conductivities was carried out as has been already described. The solutions were made up to known concentration by the exact neutralisation of known solutions of the acid and of sodium hydroxide. The latter was freshly made up from metallic sodium, and standardised with *N*/10-hydrochloric acid, using methyl-orange as indicator. In certain cases the results obtained were checked by preparing a small sample of the salt, and making up a solution gravimetrically.

The dilutions were made with water of a specific conductivity $1{\cdot}20 \times 10^{-6}$ at 25°; this value is subtracted from the conductivity obtained at each dilution (Kohlrausch, "Leitvermögen der Electrolyte," 1898, p. 91). The value of the equivalent conductivity at infinite dilution is obtained by graphical extrapolation, according to the empirical formula of Kohlrausch (*Zeitsch. Elektrochem.*, 1907, **13**, 337). From this value the velocity of the anion of each acid is found by subtracting 51·0, the value for the sodium ion.

The figures obtained agree closely, where comparison is available, with the results of Ostwald (*Zeitsch. physikal. Chem.*, 1888, **2**, 847); the greatest divergence obtained with independent series of the same salt was 0·3. Results are shown in table IV below, interpolated to the ordinary dilutions.

TABLE IV.

Equivalent Conductivity of Sodium Salts.

v.	Cyanoacetate.	*o*-Nitrobenzoate.	*o*-Chloro-benzoate.	3 : 5-Dinitro-benzoate.
16	73·6	66·9	—	—
32	77·3	70·6	71·5	68·8
64	80·3	73·6	74·3	71·3
128	82·7	76·0	76·6	73·2
256	84·4	77·9	78·4	75·0
512	85·8	79·3	79·8	76·3
1024	87·0	80·4	80·9	77·3
2048	87·9	81·2	81·8	78·1
∞	89·9	83·2	83·8	80·1
Mobility of anion	38·9	32·2	32·8	29·1

The conductivity measurements with the acids themselves are given in tables V to XI; the columns are arranged as in table I. The dissociation constant $100k_1$ is calculated with the use of that value for the equivalent conductivity at infinite dilution that gives the most satisfactory constant at high dilutions; $100m$ is the percentage dissociation obtained with this value. The constant $100k_2$ is calculated with the use of the mean value 347·2 finally taken (see p. 1293) for the velocity of the hydrogen ion.

The results obtained with each sample of water are shown in full only for cyanoacetic acid; for the other acids the figures for one sample are given in full, and the values obtained in the other cases are summarised in table XII. The effect of the different samples of water on the results was found to be the same for all the acids used, and is discussed later.

TABLE V.

Cyanoacetic Acid. Water, $0{\cdot}9 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$. ($\mathrm{H}^{\cdot} = 347{\cdot}1$).	$100k_2$. ($\mathrm{H}^{\cdot} = 347{\cdot}2$).
16·82	88·0	22·80	0·400	0·400
33·64	117·0	30·31	0·392	0·392
67·28	152·5	39·50	0·383	0·383
134·56	193·9	50·23	0·378	0·378
269·1	238·7	61·84	0·372	0·372
538·2	282·6	73·20	0·372	0·371
1076·4	320·0	82·89	0·373	0·372
2153·0	347·1	89·90	0·373	0·371
4306·0	364·8	94·52	0·378	0·376
∞	386·0	—	—	—

TABLE VI.

Cyanoacetic Acid. Water, $1·2 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$ ($H^{\cdot}=347·0$).	$100k_2$ ($H^{\cdot}=347·2$)
17·404	89·4	23·16	0·401	0·401
34·81	118·8	30·79	0·393	0·393
69·62	154·8	40·12	0·386	0·385
139·24	196·3	50·86	0·378	0·378
278·5	241·4	62·54	0·375	0·375
557·0	285·0	73·83	0·374	0·373
1114·0	321·6	83·34	0·374	0·373
2228·0	348·1	90·20	0·372	0 371
4456·0	365·3	94·67	0·377	0·373
∞	385·9	—	—	—

TABLE VII.

Cyanoacetic Acid. Water, $1·8 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$ ($H^{\cdot}=346·8$).	$100k_2$ ($H^{\cdot}=347·2$).
17·350	89·3	23·15	0·402	0·401
34·70	118·8	30·80	0·395	0·394
69·40	154·7	40·11	0·387	0·386
138·8	196·1	50·83	0·379	0·378
277·6	241·2	62·53	0·376	0·375
555·2	284·8	73·82	0·375	0·373
1110·4	321·5	83·35	0·376	0·373
2221·0	347·9	90·19	0·374	0·369
∞	385·7	—	—	—

TABLE VIII.

Cyanoacetic Acid. Water, $2·5 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$ ($H^{\cdot}=347·0$).	$100k_2$ ($H^{\cdot}=347·2$).
21·05	96·5	25·00	0·396	0·396
42·10	127·7	33·09	0·389	0·388
84·20	165·2	42·81	0·381	0·380
168·4	208·0	53·90	0·374	0·374
336·8	253·0	65·56	0·370	0·370
673·6	295·6	76·60	0·372	0·371
1347·0	330·4	85·60	0·378	0·377
2694·0	354·8	91·94	0·389	0·387
∞	385·9	—	—	—

TABLE IX.

o-*Nitrobenzoic Acid.* Water, $0·9 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$ ($H^{\cdot}=347·0$).	$100k_2$ ($H^{\cdot}=347·2$).
32	139·7	36·85	0·672	0·671
64	179·0	47·22	0·660	0·659
128	221·9	58·52	0·645	0·644
256	265·0	69·88	0·633	0·632
512	303·6	80·07	0·628	0·626
1024	333·5	87·94	0·627	0·623
2048	353·6	93·26	0·629	0·624
4096	365·3	96·36	0·618	0·609
∞	379·2	—	—	—

TABLE X.

o-Chlorobenzoic Acid. Water, $0·9 \times 10^{-6}$.

v.	μ.	100m.	100k_1. ($H^{\cdot}=347·4$).	100k_2. ($H^{\cdot}=347·2$).
150·1	134·6	35·41	0·1293	0·1294
300·2	174·0	45·76	0·1286	0·1288
600·4	218·0	57·34	0·1284	0·1286
1201·0	262·6	69·08	0·1284	0·1287
2402·0	302·1	79·45	0·1279	0·1283
4804·0	333·0	87·58	0·1286	0·1292
9608·0	353·7	93·05	0·1288	0·1298
∞	380·2	-	—	—

TABLE XI.

3:5-Dinitrobenzoic Acid. Water, $0·9 \times 10^{-6}$.

v.	μ.	100m.	100k_1. ($H^{\cdot}=346·7$).	100k_2. ($H^{\cdot}=347·2$).
254·5	175·7	46·76	0·1614	0·1607
509·0	219·0	58·28	0·1599	0·1591
1018·0	262·7	69·90	0·1594	0·1585
2036·0	301·5	80·23	0·1599	0·1586
4072·0	330·9	88·06	0·1594	0·1574
8144·0	350·7	93·34	0·1602	0·1569
∞	375·8	—	—	—

The results of the above tables, together with those obtained from the remaining experiments for *o*-nitrobenzoic acid, *o*-chlorobenzoic acid, and 3:5-dinitrobenzoic acid, are summarised in table XII. The figures shown are those values for the velocity of the hydrogen ion that give, for each particular series, the most satisfactory dissociation constant at high dilutions, as found under 100k_1 in the above tables.

TABLE XII.

Velocity of the Hydrogen Ion.

	Water, $0·9 \times 10^{-6}$.	Water, $1·2 \times 10^{-6}$.	Water, $1·8 \times 10^{-6}$.
Cyanoacetic acid	347·1	347·0	346·8
o-Nitrobenzoic acid	347·0	346·7	346·6
o-Chlorobenzoic acid	347·4	347·4	347·2
3 : 5-Dinitrobenzoic acid	346·7	346·9	346·7
Mean value..	347·0	347·0	346·8

It will be seen that the values in the above table are all in agreement within a unit; the mean value obtained from all experiments is $H^{\cdot}=347·0$. A modification in this figure, however, to the slightly higher value $H^{\cdot}=347·2$ will be shown to be necessary in a later section of the paper.

The variation in the values obtained with the use of the three different samples of water given in the table is negligible. With the first sample, which is the purest, the results obtained are more trustworthy than in the other cases, since the agreement of the values of the dissociation constant at high dilutions was here found to be more satisfactory. With the second and third samples the agreement is still good, but with the fourth sample, the ordinary distilled water of the laboratory, no agreement at all could be obtained, as will be seen in table VIII for cyanoacetic acid. The influence of the impurities in the water on the conductivity measurements is here appreciably affecting the results; the use of the fourth sample was therefore discontinued. The constant $100k_1$ in table VIII is calculated with the use of the mean value obtained from other experiments with the same acid.

From the above results it would appear that the influence of the water on the conductivity measurements obtained may be neglected, up to very high dilutions, if its specific conductivity is not greater than $1 \cdot 8 \times 10^{-6}$ at 25°. Such a general conclusion, however, cannot be drawn, for it was found that with a sample of specific conductivity only $1 \cdot 1 \times 10^{-6}$ at 25° (obtained by "rushing" a current of outside air for some time through the laboratory distilled water) no satisfactory results could be obtained in the above experiments, since the dissociation constant showed an appreciable increase at high dilutions. It seems that the nature of the impurities in the water is of importance, as well as the amount. The amount is so small that we can only, in most cases, speculate as to its nature.

We cannot be certain that the measurements obtained with dilute acid solutions are the true values unless, as stated by Kohlrausch, the water used is absolutely pure. Nevertheless, it is possible that in certain cases water with a fairly large specific conductivity will not affect the values obtained, and this would appear to be so with the water obtained by distillation from water containing Nessler's solution.

Whilst, owing to the uncertainty as to the nature of the minute trace of impurities present, we are unable to assume this with certainty, yet the satisfactory results obtained at high dilutions support the view that such is here the case.

Limits of Ostwald's Dilution Law.

It will be found on an examination of tables VI to XI that the dissociation constant $100k_1$ obtained in each case is not a true constant at the higher concentrations. The value falls steadily with dilution, and only at very high dilutions does it approach a limit. The acids employed belong, therefore, to the class of transition acids, which obey the dilution law of Ostwald only in very dilute solution.

The divergence from the law is seen to be greater as the strength of the acid increases. The difference with *o*-nitrobenzoic acid is greater than with cyanoacetic acid at the same dilution; *o*-chlorobenzoic acid and 3:5-dinitrobenzoic acid give very small divergences, and acetic acid (table II) obeys the law exactly.

The dilution law of Ostwald, which is not applicable at all to solutions of strong electrolytes, is thus applicable for weak electrolytes only within certain limits. These limits have been fully discussed by Wegscheider (*Zeitsch. physikal. Chem.*, 1909, **69**, 603); the conclusions there drawn are summarised below.

In the first place, the law holds exactly only for dilute solutions; as solutions become more concentrated the dissociation constant obtained decreases, owing to the diminished fluidity of the solution. This effect begins to be appreciable, for the majority of organic acids, between $v=16$ and $v=32$; more dilute solutions obey the dilution law exactly.

The second disturbing influence, of greater theoretical importance, is in the opposite direction, increasing the dissociation constant, and depends on the ionic concentration. The dilution law holds approximately only for solutions where the ionic concentration is less than $N/60$; if it exceeds this limit, an increasing constant is obtained; thus, for binary electrolytes, the law is approximately obeyed if $2v/m$ is greater than 120 (m being the degree of dissociation at the dilution v), and breaks down for more concentrated solutions.

In order to determine the particular point at which the law ceases to hold exactly, it is evident that accurate conductivity measurements must be made for a series of dilutions. Such experiments have been carried out by Wegscheider and Lux (*Monatsh.*, 1909, **30**, 411) in the cases of several sulphonic acids. The result obtained is that Ostwald's dilution law gives perfect agreement for solutions in which $2v/m$ exceeds 320, and approximate agreement for solutions up to $2v/m=120$.

In the conductivity measurements given above in tables I to XI, the point at which the law ceases to be applicable in each case is of interest, for comparison with the results of Wegscheider. Tables I and V to VIII (cyanoacetic acid) and table IX (*o*-nitrobenzoic acid) show clearly the divergence in the values obtained for the dissociation constant at the higher concentrations. With *o*-chlorobenzoic acid and 3:5-dinitrobenzoic acid a slight increase in the value obtained at the highest concentration is suggested, but the acids employed are so slightly soluble that solutions of a concentration at which the effect would be appreciable cannot be prepared.

The results from the above tables are given in table XIII below. v indicates the dilution at which the divergence from the law of Ostwald becomes inconsiderable, m is the degree of dissociation at that dilution, and $2v/m$ the ionic concentration.

TABLE XIII.

Limits of Ostwald's Dilution Law.

	Table.	v.	m.	$2v/m$.
1.	Cyanoacetic acid	166	0·537	618
5.	,, ,, ...	135	0·502	538
6.	,, ,, ...	139	0·509	546
7.	,, ,, ...	139	0·508	547
8.	,, ,, ...	168	0·539	623
9.	*o*-Nitrobenzoic acid	256	0·699	733

The limit is evidently higher than that obtained by Wegscheider, and the law is seen to be applicable only for solutions with an ionic concentration of less than $2v/m=600$ (approximately). This is one dilution further than the limit given by Wegscheider, but it is by no means certain that the law is exactly applicable for solutions still more dilute, although any divergence will naturally diminish with the concentration; for we have, in the above tables, arbitrarily fixed the value for the equivalent conductivity at infinite dilution so as to obtain a satisfactory dissociation constant at high dilutions. We have no proof that a value, higher by a few tenths of a unit, which would give at these dilutions a still slowly decreasing constant, may not be nearer to the truth.

A modification of Ostwald's dilution law, so that it will apply to the more concentrated solutions, would enable us to calculate what effect this second disturbing influence exerts on the constant at high dilutions. Such a formula is developed below.

The Dissociation of Transition Electrolytes.

In dilute solution (v greater than 16) very weak electrolytes are found to follow exactly the dilution law of Ostwald, $m^2/(1-m)v=k$, as will be seen for acetic acid in tables II to III. Strong electrolytes obey approximately the empirical formula of van't Hoff, $m^3/(1-m)^2v=C$, which may be written in the form $m^2/(1-m)v=c(1-m)/m$. It is therefore to be expected that the intermediate or transition electrolytes will obey an intermediate formula, for example,

$$m^2/(1-m)v=k+c(1-m)/m\,;$$

and the agreement of this with the experimental data is shown in the tables which follow.

The values for $m^2/(1-m)v$ that are obtained for solutions of an acid by the above formula decrease with the concentration of the solution, and ultimately attain a limiting value k_∞ at infinite dilution. The value of k_∞ is found from the conductivity results of a series of dilutions by the use of that particular value for the velocity of the hydrogen ion that gives values, for $m^2/(1-m)v$, slowly falling as dilution increases, and ultimately approaching (so far as can be perceived within experimental error) a limiting value. The value of c is obtained by trial from the experimental results.

In the results shown previously in table XII, that velocity for the hydrogen ion was taken in each series that gave constant values for $m^2/(1-m)v$ at high dilutions. The mean value deduced was $\mathrm{H}^{\cdot}=347{\cdot}0$. The value required to give slowly-falling figures for $m^2/(1-m)v$ at high dilutions is very slightly higher in each series; the mean value required is $\mathrm{H}^{\cdot}=347{\cdot}2$. In the following tables, therefore, k_∞ is obtained with the use of this value, $\mathrm{H}^{\cdot}=347{\cdot}2$.

Table XIV gives the results for cyanoacetic acid obtained from table V. The first column shows the dilution, the second the ratio of the non-ionised to the ionised part. In the third column the values calculated from the formula for the dissociation constant at each dilution are given. These are compared with the experimental values, $100m^2/(1-m)v$, obtained with the use of the two different values for the velocity of the hydrogen ion referred to above. These experimental figures are the same as were expressed by $100k_1$ and $100k_2$ in table V. Finally, the figures under $100k$ show the value obtained at each dilution from the experimental results in the preceding column ($\mathrm{H}^{\cdot}=347{\cdot}2$) by subtracting the value of $c(1-m)/m$. The constancy of the values obtained in the last column therefore shows the agreement of the formula with the experimental results.

TABLE XIV.

Cyanoacetic Acid (see table V). $k_\infty=0{\cdot}00368$; $c=0{\cdot}00010$.

v.	$(1-m)/m$.	$100(k_\infty+c(1-m)/m$.	$100m^2/(1-m)v$ ($\mathrm{H}^{\cdot}=347{\cdot}1$).	$100m^2/(1-m)v$ ($\mathrm{H}^{\cdot}=347{\cdot}2$).	$100k$.
16·82	3·39	0·402	0·400	0·400	0·366
33·64	2·30	0·391	0·392	0·392	0·369
67·28	1·53	0·383	0·383	0·383	0·368
134·56	0·99	0·378	0·378	0·378	0·368
269·1	0·62	0·374	0·372	0·372	0·366
538·2	0·37	0·372	0·372	0 371	0·367
1076·4	0·21	0·370	0·373	0·371	0·369
2153·0	0·11	0·369	0·373	0·371	0·370
4306·0	0·06	0·369	0·378	0·376	0·375
∞	0·00	0·368	—	—	—

The agreement between the calculated and experimental values is seen to be very satisfactory throughout the whole range of dilutions. Further examples of the agreement of the formula with the previous results are shown in its application to *o*-nitrobenzoic acid and 3:5-dinitrobenzoic acid in tables XV and XVI below.

TABLE XV.

o-*Nitrobenzoic Acid* (see table IX). $k_\infty = 0{\cdot}00620$; $c = 0{\cdot}00032$.

v.	$(1-m)/m$.	$100(k_\infty + c(1-m)/m$.	$100m^2/(1-m)v$ (H˙ = 347·0).	$100m^2/(1-m)v$ (H˙ = 347·2).	$100k$.
32	1·71	0·675	0·672	0·671	0·616
64	1·12	0·656	0·660	0·659	0·623
128	0·71	0·643	0·645	0·644	0·621
256	0·43	0·634	0·633	0·632	0·618
512	0·25	0·628	0·628	0·626	0·618
1024	0·14	0·624	0·627	0·623	0·619
2048	0·07	0·622	0·629	0·624	0·622
4096	0·04	0·621	0·618	0·609	0·608
∞	0·00	0·620	—	—	—

TABLE XVI.

3:5-*Dinitrobenzoic Acid* (see table XI). $k_\infty = 0{\cdot}001570$; $c = 0{\cdot}000030$.

v.	$(1-m)/m$.	$100(k_\infty + c(1-m)/m$.	$100m^2/(1-m)v$ (H˙ = 346·7).	$100m^2/(1-m)v$ (H˙ = 347·2).	$100k$.
254·5	1·14	0·1604	0·1614	0·1607	0·1573
509·0	0·72	0·1592	0·1599	0·1591	0·1569
1018·0	0·43	0·1583	0·1594	0·1585	0·1572
2036·0	0·25	0·1577	0·1599	0·1586	0·1579
4072·0	0·14	0·1574	0·1594	0·1574	0·1570
8144·0	0·07	0·1572	0·1602	0·1569	0·1567
∞	0·00	0·1570	—	—	—

The agreement of the formula with the results of experiment is for both acids very satisfactory. With the very dilute solutions the values for $m^2/(1-m)v$ obtained with the use of H˙ = 347·2 are seen to be in better agreement with the formula than those given in the preceding column. The results obtained in tables XIV to XVI, therefore, lead us to the conclusion that the value for the velocity of the hydrogen ion is not that required to give constant values for $m^2/(1-m)v$ at high dilutions, but that which gives values slowly decreasing and ultimately reaching a limit.

The method employed in the first part of the paper to obtain the velocity of the hydrogen ion is thus found to give results a little below this required value. The mean value H˙ = 347·0 previously deduced has therefore been amended to the slightly higher figure of H˙ = 347·2.

The values for the velocity of the hydrogen ion obtained in table XII are all in agreement within a unit. If the two purest samples of water only are considered, the agreement is slightly better; results are concordant within 0·2 to 0·4 for each acid, whilst the greatest divergence between those for different acids is 0·7. The value for the velocity of the hydrogen ion, amended from the above results, can therefore be stated as 347·2 ± 0·4 at 25°. At 18° the value becomes, with the use of the temperature-coefficient given by Kohlrausch (*Zeitsch. Elektrochem.*, 1902, **8**, 290), $H^{\cdot} = 313·9$.

The General Application of the above Dissociation Formula.

It has been remarked that the divergence from the simple dilution law increases with the strength of the acid used, and in tables XIV to XVI it is seen that c does increase with k. With very weak acids, therefore, it will be impossible to notice any divergence from Ostwald's dilution law in dilute solutions; this is so in the case of acetic acid, as shown in table II. With stronger acids, however, the variation in the values of the dissociation constant with dilution will be much greater; an example—trichlorobutyric acid—is given in table XVII below.

The figures given in the table differ materially from those of Ostwald (*Zeitsch. physikal. Chem.*, 1888, **3**, 194). This is probably due to the removal of impurities in the method of purification adopted. The acid dissolves readily on treatment with a small quantity of water, but leaves a less soluble residue. This was collected, and the clear filtrate carefully evaporated to dryness. The acid was then dissolved in light petroleum, and recrystallised several times.

TABLE XVII.

Trichlorobutyric Acid. $k_\infty = 0·095$; $c = 0·35$.

v.	μ.	$(1-m)/m$.	$100(k_\infty + c(1-m)/m$.	$100m^2/(1-m)v$.	$100k$.
38·63	326·4	0·152	14·8	14·8	9·5
53·98	336·0	0·119	13·7	13·9	9·7
77·26	343·9	0·093	12·7	12·7	9·5
107·96	350·4	0·073	12·1	11·8	9·2
154·5	357·0	0·054	11·4	11·5	9·6
215·9	361·2	0·041	10·9	10·9	9·5
309·0	365·1	0·030	10 5	10·5	9·5
431·8	368·2	0·021	10·2	10·7	10·0
618·0	370·9	0·014	10·0	11·6	11·1
∞	(376·0)	0·000	9·5	—	—

The value for the equivalent conductivity at infinite dilution is only approximate, being obtained from the number of atoms in the molecule by Ostwald's method (*Zeitsch. physikal. Chem.*, 1888, **2**, 840). In view of the proximity of the measurements to this uncertain value, the agreement throughout the series between the calculated and experimental figures is very satisfactory.

A complete series of measurements with a still stronger acid, namely, *p*-toluenesulphonic acid, has been carried out by Wegscheider and Lux (*Monatsh.*, 1909, **30**, 436); the agreement of the formula with their results is shown in the following table. In the calculation of the results from the experimental data the value $\mathrm{H}^{\cdot} = 347{\cdot}2$ is employed.

TABLE XVIII.

p-*Toluenesulphonic Acid.* $k_\infty = 0{\cdot}090$; $c = 5{\cdot}6$.

v	25·00	32·66	44·44	51·02	59·17	69·44	82·64	100·0	123·4
$100(k_\infty + c(1-m)/m)$	50·4	45·4	39·8	37·0	34·8	32·0	29·7	28·0	25·8
$100m^2/(1-m)v$	50·6	44·3	38·7	37·2	35·2	34·0	31·8	28·7	26·5
$100k$	9·2	7·9	7·9	9·2	9·4	11·0	11·1	9·7	9·7

v	156·3	204·1	277·7	330·6	400·0	493·8	625·0	816·8	1111	1600	∞
$100(k_\infty + c(1-m)/m)$	24·1	21·9	19·6	18·5	17·4	16·2	15·2	14·0	12·9	11·8	9·0
$100m^2/(1-m)v$	22·6	21·0	18·3	17·4	16·8	16·0	14·9	13·9	13·0	13·1	—
$100k$	7·5	8·1	7·7	7·9	8·4	8·8	8·7	8·9	9·1	10·3	—

The acid is so highly dissociated that the differences between the calculated and experimental values are all within the limits of experimental error. The formula is found to hold throughout a five-fold change in the values obtained by experiment for $m^2/(1-m)v$.

The agreement of the formula for an acid of another type—phosphoric acid—is shown in table XIX. The results are calculated with the use of the value $\mathrm{H}^{\cdot} = 347{\cdot}2$ by interpolation from the figures given by Rothmund and Drucker for the experiments of Loomis (*Zeitsch. physikal. Chem.*, 1903, **46**, 850).

TABLE XIX.

Phosphoric Acid. $k_\infty = 0{\cdot}0070$; $c = 0{\cdot}0013$.

v	16	32	64	128	256	512	1024
$100(k_\infty + c(1-m)/m)$	0·97	0·89	0·83	0·78	0·75	0·73	0·72
$100m^2/(1-m)v$	0·96	0·87	0·82	0·81	0·76	0·77	0·69
$100k$	0·69	0·68	0·69	0·73	0·71	0·74	0·67

The agreement between the calculated and observed figures is again satisfactory. The second and third dissociations of the acid are evidently too weak to affect the results, even at the highest dilutions given.

The stronger inorganic acids, such as hydrochloric acid, are of a different type. The values obtained for $m^2/(1-m)v$ certainly do fall away, as dilution is increased, to a limiting value k_∞, but that limiting value is zero. The results for hydrochloric acid are given in table XX below. The measurements of Goodwin and Haskell at 18° (*Zeitsch. physikal. Chem.*, 1905, **52**, 630) are employed, the value $\mathrm{H}^{\cdot} = 313{\cdot}9$ being used in the calculation of the degree of dissociation at each dilution.

TABLE XX.

Hydrochloric Acid. $k_\infty = 0·00$; $c = 13·4$.

v	20	33·3	50	100	200	500	667	1000
$100(k_\infty + c(1-m)/m)$	78·5	62·4	50·9	36·4	24·5	14·8	13·5	12·4
$100m^2/(1-m)v$	80·6	61·5	50·6	35·6	26·9	18·1	14·7	10·6
$100k$	+2·1	−0·9	−0·3	−0·8	+2·4	+3·3	+1·2	−1·8

v	1333	2000	4000	∞
$100(k_\infty + c(1-m)/m)$	11·4	8·5	6·3	0·0
$100m^2/(1-m)v$	8·7	7·8	5·2	—
$100k$	−2·7	−0·7	−1·3	—

The conductivity measurements are all so very near to the value at infinite dilution that the possible degree of error in the above calculations is considerable; the agreement in all cases is within the limits of experimental error.

In conclusion, the dissociation formulæ of a number of typical electrolytes, calculated from the available experimental data, are collected in table XXI.

TABLE XXI.

Dissociation of Electrolytes.

Dissociation formula: $m^2/(1-m)v = k + c \, . \, (1-m)/m$.

Acid.	Observer.	k.	c.
Acetic	Kendall	0·0000185	—
o-Bromobenzoic	Ostwald	0·00140	0·00004
p-Nitrophenylglycollic	,,	0·00149	0·00004
3 : 5-Dinitrobenzoic	Kendall	0·00157	0·00003
Aniline-*o*-sulphonic	Ostwald	0·00310	0·00015
Cyanoacetic	Kendall	0·00368	0·00010
Trichlorolactic	Ostwald	0·00440	0·00020
o-Nitrobenzoic	Kendall	0·00620	0·00032
Phosphoric	Loomis	0·0070	0·0013
5-Bromo-2-nitrobenzoic	Ostwald	0·012	0·007
4 : 6-Dibromoaniline-3-sulphonic	,,	0·019	0·030
Dichloroacetic	Walker	0·0316	0·080
β-Resorcylic	Ostwald	0·032	0·075
Trichlorobutyric	Kendall	0·095	0·35
p-Toluenesulphonic	Wegscheider and Lux	0·090	5·6
β-Naphthalenesulphonic	,, ,,	0·120	6·6
Hydrochloric	Goodwin and Haskell	—	13·4

It is evident from the above figures that c increases with k, and increases much more rapidly. Ostwald's dilution law is a limiting case of the formula, since with very weak electrolytes c is so nearly equal to zero that the dissociation constant is practically unaffected. Similarly, van't Hoff's empirical law for strong electrolytes is a special case of the above formula, where $k = 0$. The dissociation formula given above is therefore applicable to all acids. For salts, however, the divergences from the simple van't Hoff formula are beyond the limits of experimental error, even in dilute solution.

It does not seem possible to establish a connexion between the constants k and c. In the above table c is roughly proportional to k^2 for the weaker acids, but this relation cannot be general, since for strong electrolytes c is large whilst k is zero. Finally, it may be noted that the dissociation of transition acids can in no way be expressed by a formula intermediate between Ostwald's dilution law and Rudolphi's formula for strong electrolytes.

Summary of Results.

The following method has been employed for the determination of the velocity of the hydrogen ion, and has been found to give concordant results. If conductivity measurements are carried out with a series of very dilute solutions of a weak acid, the values obtained for the dissociation constant vary greatly according to the value for the velocity of the hydrogen ion used in the calculation of the equivalent conductivity at infinite dilution. With acids of a certain range of strength ($100k$ between 0·1 and 1·0) it has been found that a satisfactory dissociation constant at very high dilutions can only be obtained with the use of one particular value for the velocity of the hydrogen ion. The mean of the values deduced from a number of experiments with different acids was $\text{H}^{\cdot}=347{\cdot}0$. A slight modification of this result was afterwards found necessary, the figure finally obtained being $\text{H}^{\cdot}=347{\cdot}2$ at 25° (or 313·9 at 18°), with a maximum divergence of $\pm 0{\cdot}4$.

It has been found that the dilution law of Ostwald is not exactly obeyed by the acids employed in the above determination, even in very dilute solution. A formula for the dissociation of these acids, $m^2/(1-m)v=k+c(1-m)/m$, where k and c are constants for each acid, has been developed, and found to be in perfect agreement with the experimental data. For the transition acids in general, c increases with k.

This formula has been extended to acids of all types. Ostwald's dilution law for weak electrolytes is a limiting case, since as k decreases c approaches zero; van't Hoff's formula for strong electrolytes is a special case, where k is zero. The above dissociation holds, therefore, within the limits of experimental error for all acids.

I desire to express my thanks to Professor Walker for the interest he has taken in this research, and for advice during its progress.

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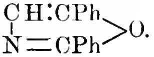
CXXXIX.—*Some Derivatives of Oxazole.*

By JOSEPH LISTER and ROBERT ROBINSON.

IN a previous communication (Robinson, Trans., 1909, **95**, 2167) a method of synthesis of oxazole derivatives was described, depending on the dehydration of acylated amino-ketones by means of sulphuric acid; thus ω-benzoylaminoacetophenone, $COPh\cdot CH_2\cdot NHBz$, is readily changed by sulphuric acid to 2:5-diphenyloxazole,

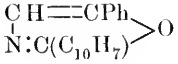


$$\begin{matrix} CH{:}CPh \\ | \\ N{=}CPh \end{matrix}\!\!>O.$$

Shortly afterwards Gabriel (*Ber.*, 1910, **43**, 143, 1283) showed that the action of phosphorus pentachloride and of phosphorus pentasulphide on substances of the type of ω-benzoylaminoacetophenone is to produce the corresponding oxazoles and thiazoles respectively. Gabriel also introduced a method of acylating amino-ketones by means of the acid chloride in acetic acid solution and in presence of sodium acetate, which is extremely convenient in the case of solid acid chlorides (see pp. 1308, 1309). The substances described in the present paper were prepared for the most part by the original process, although Gabriel's method of acylation was employed in one or two cases. The amino-ketones used were ω-aminoacetophenone, α-aminopropiophenone, ω-amino-*p*-methoxyacetophenone, and α-naphthyl aminomethyl ketone. The acid radicles introduced were, in the case of ω-aminoacetophenone, *o*-, *m*-, and *p*-toluoyl, *o*-chlorobenzoyl, anisoyl, cinnamoyl, *o*- *m*-, and *p*-nitrobenzoyl, and α-naphthoyl; in the case of ω-amino-*p*-methoxyacetophenone, benzoyl and cinnamoyl; whilst oxazole derivatives were obtained from the benzoyl derivatives only of α-aminopropiophenone and α-naphthyl aminomethyl ketone. In every case the oxazole was rapidly formed when the amino-ketone was dissolved in cold sulphuric acid. On dilution with water the oxazole salt was decomposed and the free oxazole obtained, usually as a crystalline precipitate, and most of the substances crystallised best from light petroleum. These compounds were synthesised in the first instance in order that their fluorescence and ultraviolet absorption might be closely investigated, preliminary observations having indicated that the derivatives of oxazole present features of interest in these directions. This research has now been undertaken by Mr. F. R. Lankshear, and we therefore, at this stage, mention only those properties which can be observed visually. The violet to blue fluorescence of the oxazoles is intensified by methyl, methoxy-, and amino-groups, and to a very much greater extent when the phenyl groups are replaced by styryl or naphthyl; thus, as surmised in the previous paper (*loc. cit.*), the longer the chain of conjugated double linkings contained in the molecule the more intense is the fluorescence. When, however, nitro-groups are introduced into diphenyloxazole, the substance is no longer fluorescent, a fact which has been previously observed in other quite different cases. The more strongly fluorescent oxazole derivatives have absorption bands which verge on the visible region of the spectrum, and in some cases are actually in it. These compounds are on the border of colour, and this point is well illustrated by a comparison of the two phenylnaphthyloxazoles.

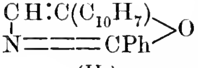
5-Phenyl-2-α-naphthyloxazole (I) was obtained by the action of sulphuric acid on ω-1-naphthoylaminoacetophenone (p. 1306), whilst 2-phenyl-5-α-naphthyloxazole (II) was obtained by the same process applied to α-naphthyl benzoylaminomethyl ketone (p. 1308).

(I) is yellow and extremely fluorescent in the solid state, or in solution, but, on the other hand, (II) is colourless and fluorescent only in solution:



$$\left.\begin{array}{l} CH{=\!=}CPh \\ N{:}C(C_{10}H_7) \end{array}\right>O$$

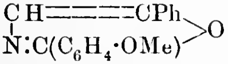
(I.)



$$\left.\begin{array}{l} CH{:}C(C_{10}H_7) \\ N{=\!=\!=}CPh \end{array}\right>O$$

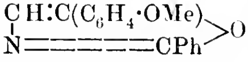
(II.)

The difference in constitution between these two substances appears slight, but the effect of this interchange of groups is nevertheless considerable. That the positions 2- and 5- in the oxazole ring have a different effect on groups attached to them, is shown by the fact that 2:5 diphenyloxazole can be nitrated so as to yield 2-phenyl-5-nitrophenyloxazole unmixed with the isomeric 5-phenyl-2-nitrophenyloxazole. The proof of this statement is given on p. 1313. Attention may be directed here to the peculiar properties of nitrodiphenyloxazoles and their derivatives. These compounds are obtained by condensing ω-aminoacetophenone with *o*-, *m*-, and *p*-nitrobenzoyl chlorides, and subjecting the ω-nitrobenzoylaminoacetophenones so formed to the dehydrating action of concentrated sulphuric acid. The ortho-compound melts at 118°, the meta at 149°, and the para at 204°. The latter differs from the other isomerides, not only because of its high melting point, but also on account of its sparing solubility and bright yellow colour. The colour is observed in the solid state only, and the substance is not more coloured in solution than the *o*- and *m*-isomerides. Intensely coloured diazo-salts of great stability are obtained by the action of nitrous acid on the amines produced by reduction of these nitro-compounds. They readily yield *iso*diazotates, and little or no combination with β-naphthol occurs in strongly alkaline solution. The stability and colour of the diazonium salts may be ascribed to the mutual influence of the residual affinities of the diazo- and oxazole complexes. 5-Phenyl-2-styryloxazole and 5-anisyl-2-styryloxazole have been prepared by the synthetical method described on p. 1303, and their melting points are so much higher than those given by Minovici (*Ber.*, 1896, **29**, 2102) for substances which he described as having these constitutions and prepared by the condensation of benzaldehyde- and anisaldehyde-cyanohydrins respectively with cinnamaldehyde, that we have little doubt, as indeed our repetition of his experiments has indicated, that this author was in these cases dealing with a mixture of substances extremely difficult to separate and purify by the methods he employed. These results with styryl compounds induced us to test the application of Minovici's method of synthesis in other cases. He obtained 5-phenyl-2-anisyloxazole (III) (*Ber.*, 1896, **29**, 2099) by the condensation of benzaldehydecyanohydrin and anisaldehyde by means of hydrochloric acid, and in a similar manner 2-phenyl-5-anisyloxazole (IV) from anisaldehyde and benzaldehydecyanohydrin. We have obtained substances agreeing in melting point and other properties with the substances (III) and (IV) of Minovici, by the action of sulphuric acid on ω-anisoylaminoacetophenone (V) and ω-benzoylamino-*p*-methoxyacetophenone (VI) respectively. The styryl compounds constitute, therefore, a special case, and there can be little doubt that the condensation between cyanohydrins and aldehydes of the aromatic series occurs as has always been supposed:



$$\left.\begin{array}{l}\mathrm{CH{=\!=\!=\!=}CPh}\\ \mathrm{N{:}C(C_6H_4{\cdot}OMe)}\end{array}\right>\mathrm{O}$$

(III.)



$$\left.\begin{array}{l}\mathrm{CH{:}C(C_6H_4{\cdot}OMe)}\\ \mathrm{N{=\!=\!=\!=\!=\!=}CPh}\end{array}\right>\mathrm{O}$$

(IV.)

$COPh{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$ (V.)

$MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}NHBz$ (VI.)

EXPERIMENTAL.

ω-Toluoylaminoacetophenones, $COPh{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CH_3$.

These compounds were prepared by acylating ω-aminoacetophenone with *o*-, *m*-, and *p*-toluoyl chlorides according to the method previously employed for the benzoylation of the base (Robinson, *loc. cit.*).

ω-Aminoacetophenone stannichloride (9 grams) was dissolved in hot water (150 c.c.), and the solution cooled until the salt began to separate. Toluoyl chloride (12 grams) and finally with very vigorous shaking, aqueous potassium hydroxide (30 grams in 50 c.c.) were then added. The amide, which separated in the solid state, was collected and freed from a certain small amount of oily impurity by contact with porous porcelain. The yield is very good when the operations are carried out quickly, but it is easy to be unsuccessful in these and similar preparations, and to produce a considerable amount of orange-red colouring matter if the conditions are not closely observed and followed.

Ortho-compound.—This was recrystallised from ether, and obtained in short, colourless prisms melting at 97°. It is readily soluble in chloroform, moderately so in benzene or alcohol, and sparingly so in cold ether or boiling light petroleum:

0·1712 gave 0·4760 CO_2 and 0·0936 H_2O. $C=75·8$; $H=6·0$.
$C_{16}H_{15}O_2N$ requires $C=75·9$; $H=5·9$ per cent.

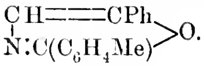
Meta-compound.—The solubility relations of this substance are similar to those of the preceding compound. It was purified by crystallisation from benzene, from which it separates in colourless needles melting at 118—119°:

0·2520 gave 12·1 c.c. N_2 at 15° and 745 mm. $N=5·6$.
$C_{16}H_{15}O_2N$ requires $N=5·5$ per cent.

Para-compound.—After crystallisation first from benzene and light petroleum (b. p. 56—60°) and then from dry ether, the substance was obtained in long needles melting at 125°. It is rather less soluble than the corresponding *o*- and *m*-compounds:

0·1312 gave 0·3641 CO_2 and 0·0694 H_2O. $C=75·7$; $H=5·9$.
$C_{16}H_{15}O_2N$ requires $C=75·9$; $H=5·9$ per cent.

5-*Phenyl*-2-o-, m-, *and* -p-*tolyloxazoles*,



$$\left.\begin{matrix}\mathrm{CH{=\!=\!=}CPh}\\ \mathrm{N{:}C(C_6H_4Me)}\end{matrix}\right>\mathrm{O.}$$

On dehydration by means of concentrated sulphuric acid, each of the ω-toluoylaminoacetophenones furnishes the corresponding phenyltolyloxazole, and the procedure is identical for the three substances. The amide (4 grams) is dissolved in concentrated sulphuric acid (20 c.c.), and the solution, which acquires an intense blue fluorescence, allowed to remain for five minutes. On pouring into water the oxazole sulphate is decomposed, and the free base obtained in a crystalline condition. The yield approaches closely to that demanded by theory. After collection, the dried substance is crystallised from light petroleum (b. p. 60—70°).

Ortho-compound.—In common with the meta- and para-derivatives, this compound is readily soluble in the usual organic solvents with the exception of light petroleum, and its solutions possess a faint blue fluorescence in ordinary light, brilliant, however, in strong sunlight, the light of burning magnesium, or the electric arc. The substance forms clusters of slender needles, and melts at 93°:

0·1723 gave 0·5147 CO_2 and 0·0882 H_2O. C = 81·5; H = 5·7.
0·2405 „ 12·6 c.c. N_2 at 16° and 750 mm. N = 6·1.
$C_{16}H_{13}ON$ requires C = 81·7; H = 5·5; N = 5·9 per cent.

The *picrate* * is readily prepared by dissolving the oxazole in alcoholic picric acid solution. It crystallises from alcohol in yellow needles melting at 170°:

0·1405 gave 14·6 c.c. N_2 at 16° and 756 mm. N = 12·2.
$C_{16}H_{13}ON,C_6H_3O_7N_3$ requires N = 12·1 per cent.

Meta-compound.—The fluorescence of this substance is weak under ordinary conditions. In general properties it resembles very much the isomeric compounds. It crystallises in needles, and melts at 101—102°:

0·1621 gave 0·4841 CO_2 and 0·0813 H_2O. C = 81·5; H = 5·6.
$C_{16}H_{13}ON$ requires C = 81·7; H = 5·5 per cent.

Para-compound.—The substance crystallises in colourless, nodular masses of small prisms, melting at 77°:

0·1162 gave 0·3465 CO_2 and 0·0495 H_2O. C = 81·3; H = 4·7.
$C_{16}H_{13}ON$ requires C = 81·7; H = 5·5 per cent.

Picrate.—The oxazole is readily soluble in alcohol, and on the addition of picric acid yields the picrate, which is readily soluble in hot alcohol, and crystallises on cooling in golden-yellow needles melting, with slight previous shrinking, at 193°.

ω-Chlorobenzoylaminoacetophenone, $COPh\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4Cl$.

This compound was prepared from ω-aminoacetophenone stannichloride and *o*-chlorobenzoyl chloride by the Schotten-Baumann method employed for the preparation of the toluoylaminoacetophenones (see above).

The solid product was washed with ether, whereby a considerable amount of impurity was removed, and then crystallised from benzene. The colourless needles melted at 113°:

0·1661 gave 0·0866 AgCl. Cl = 12·9.
$C_{15}H_{12}O_2NCl$ requires Cl = 13·0 per cent.

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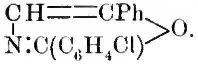
* Owing to a clerical error the melting point of 5-phenyl-2-benzyloxazole is incorrectly stated in the previous communication (*loc. cit.*). This substance crystallises from alcoholic picric acid in yellow needles melting at 160°.

5-*Phenyl*-2-o-*chlorophenyloxazole*,



$$\left.\begin{matrix}CH{=\!=}CPh\\ |\quad\quad\quad\\ N{:}C(C_6H_4Cl)\end{matrix}\right\rangle O.$$

The preceding ketone is less readily converted into an oxazole by means of concentrated sulphuric acid than are the toluoylaminoacetophenones, and in order to complete the change the solution of the substance in ten times its weight of sulphuric acid must be allowed to remain for at least half an hour. On then pouring into water the free oxazole is obtained. It is collected and crystallised from boiling light petroleum (b. p. 60—70°), from which it separates in clusters of needles, but it may also be crystallised in the form of stout prisms from ether. The compound melts at 80—81°, is readily soluble in organic solvents, and the solutions show very faint blue fluorescence:

0·3212 gave 0·1772 AgCl. Cl = 13·7.

$C_{15}H_{10}ONCl$ requires Cl = 13·7 per cent.

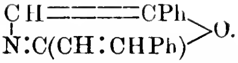
ω-*Cinnamoylaminoacetophenone*, $COPh\cdot CH_2\cdot NH\cdot CO\cdot CH{:}CHPh$.

ω-Aminoacetophenone stannichloride (10 grams) was dissolved in warm water (150 c.c.), and molten cinnamoyl chloride (10 grams) added. The liquid was cooled with water and vigorously shaken, and when the cinnamoyl chloride showed signs of crystallisation, potassium hydroxide (35 grams), dissolved in water, was quickly poured into the mixture. Sometimes the chloride did not crystallise even when quite cold, and in this case an increased yield was obtained. The product was a red, viscid mass, which was extracted from the yellow aqueous solution with ether. The extract was washed with dilute hydrochloric acid, with sodium carbonate solution, and with much water, and then dried with calcium chloride. Most of the ether was removed by distillation, when, on allowing to remain in the cold, crystals separated from the solution. These have a greenish tinge, which in solution becomes rose-red, and this could only be removed by crystallisation from benzene and alcohol alternately. The substance was finally obtained in the form of shining leaflets melting at 139°, rather sparingly soluble in cold benzene or alcohol and in ether, but readily so in hot benzene and alcohol, or in chloroform:

0·1189 gave 0·3339 CO_2 and 0·0584 H_2O. C = 76·6; H = 5·6.

$C_{17}H_{15}O_2N$ requires C = 77·0; H = 5·7 per cent.

5-Phenyl-2-styryloxazole,



$$\left.\begin{array}{l}CH{=\!=\!=\!=}CPh\\ \overset{|}{N}{:}C(CH{:}CHPh)\end{array}\right>O.$$

ω-Cinnamoylaminoacetophenone is very readily converted into the corresponding oxazole. The substance is treated as in other cases with concentrated sulphuric acid, and complete solution occurs in a few minutes. The oxazole separates on the addition of water, and crystallises from light petroleum (b. p. 56—60°) in radiating bunches of needles melting at 106°. It is readily soluble in all organic solvents, and the solutions show intense bluish-violet fluorescence:

0·1226 gave 0·3705 CO_2 and 0·0616 H_2O. C=82·4; H=5·6.

$C_{17}H_{13}ON$ requires C=82·6; H=5·3 per cent.

Minovici (*Ber.*, 1896, **29**, 2102), by the condensation of mandelonitrile and cinnamaldehyde by means of hydrochloric acid, obtained an oxazole derivative, to which he ascribed the constitution possessed by the present 5-phenyl-2-styryloxazole. Since, however, Minovici's product melted at 62°, this conclusion was incorrect. It is very probable that Minovici's substance was a mixture of diphenyloxazole, phenylstyryloxazole, and distyryloxazole, all of which could be produced in the reaction, since it would be very difficult to avoid partial decomposition of the cyanohydrin of benzaldehyde and partial formation of that of cinnamaldehyde. Moreover, such a mixture would not be separated into its constituents by the methods employed. It is hoped that an account will shortly be published of the synthesis of 2-phenyl-5-styryloxazole, a substance which melts at 88°, and has been isolated from the products of the condensation of cinnamaldehydecyanohydrin and benzaldehyde with hydrochloric acid, as well as produced by synthesis.

ω-(β)-Phenylpropionylaminoacetophenone,
$COPh{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH_2Ph$.

β-Phenylpropionyl chloride (5 grams) was mixed with an ice-cold aqueous solution of ω-aminoacetophenone stannichloride (11·5 grams), and with vigorous stirring potassium hydroxide (30 grams) in water (50 c.c.) was then added. The solid product was collected and crystallised first from ether, in which it is rather more soluble than is usual for this class of compound, and then from light petroleum. The substance occurs in colourless plates melting at 101°, and is very readily soluble in the ordinary organic solvents:

0·1711 gave 0·4777 CO_2 and 0·1000 H_2O. C=76·1; H=6·5.

$C_{17}H_{17}O_2N$ requires C=76·4; H=6·4 per cent.

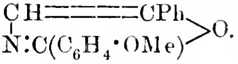
This substance is peculiar in that it is precipitated unchanged from sulphuric acid solution by water. It was not found possible to obtain the oxazole, since decomposition ensued when the solution was heated. This behaviour is all the more remarkable when it is compared with that of the corresponding cinnamoyl (see above) and phenacetyl (Robinson, *loc. cit.*) compounds, which are quantitatively converted into oxazoles by cold sulphuric acid.

ω-Anisoylaminoacetophenone, $COPh\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot OMe$.

The preparation of this compound was similar in almost all its details to that of cinnamoylaminoacetophenone (see above). The crystallisation was accomplished as in that case, first from ether and afterwards from benzene. The substance is very readily soluble in the hot solvent, and rather sparingly so in the cold. It forms colourless prisms melting at 141°:

0·1682 gave 0·4400 CO_2 and 0·0845 H_2O. C=71·3; H=5·6.
$C_{16}H_{15}O_3N$ requires C=71·4; H=5·6 per cent.

5-*Phenyl-2-anisyloxazole*,



$$\left.\begin{array}{l}\mathrm{CH{=\!=\!=\!=}CPh}\\ \mathrm{N{:}C(C_6H_4{\cdot}OMe)}\end{array}\right\rangle \mathrm{O.}$$

The production of the oxazole is complete when ω-anisoyl aminoacetophenone is dissolved in sulphuric acid. As soon as complete solution has been obtained, water is added, and the product collected and crystallised two or three times from hot light petroleum (b. p. 50—60°), in which it is moderately soluble. The substance forms clusters of long needles melting at 101°, very soluble in benzene, and somewhat less so in alcohol. Although the solutions are decidedly fluorescent, this property is not nearly so marked as in the case of the phenylstyryloxazole previously described:

0·1539 gave 0·4305 CO_2 and 0·0686 H_2O. C=76·3; H=5·0.
$C_{16}H_{13}O_2N$ requires C=76·5; H=5·2 per cent.

The *picrate* is readily prepared by mixing alcoholic solutions of the components. It crystallises in yellow prisms melting at 191°:

0·2000 gave 19·4 c.c. N_2 at 20° and 761 mm. N=11·3.
$C_{16}H_{13}O_2N,C_6H_3O_7N_3$ requires N=11·6 per cent.

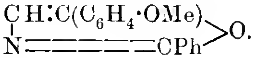
This oxazole is therefore identical with that which Minovici (*loc. cit.*) prepared from benzaldehyde and anisaldehydecyanohydrin, to which he ascribed the melting point 99° (picrate, 195°).

ω-Benzoylamino-p-*methoxyacetophenone*,
$MeO\cdot C_6H_4\cdot CO\cdot CH_2\cdot NHBz$.

ω-Amino-*p*-methoxyacetophenone stannichloride (10 grams) was suspended in water (100 c.c.), vigorously stirred with benzoyl chloride (12 grams), and cooled by ice. Potassium hydroxide (60 grams) in water (100 c.c.) was then added, and the stirring continued during two hours. The solid was collected, drained on porous porcelain, and crystallised, first from ether and then from benzene, from which it separates in silky needles melting at 113°:

0·2135 gave 10·0 c.c. N_2 at 16° and 758 mm. N=5·5.
$C_{16}H_{15}O_3N$ requires N=5·2 per cent.

2-Phenyl-5-anisyloxazole,



$$\left.\begin{array}{l}\mathrm{CH{:}C(C_6H_4{\cdot}OMe)} \\ \mathrm{N{=\!=\!=\!=\!=}CPh}\end{array}\right>\mathrm{O}.$$

ω-Benzoylamino-*p*-methoxyacetophenone yields this oxazole on treatment with sulphuric acid, but the process is not so smooth as in other cases. The amide was dissolved in five times its weight of cold sulphuric acid, and allowed to remain during five minutes. On pouring into water, a green precipitate was obtained, from which hot light petroleum extracts the oxazole and leaves an insoluble residue, which probably consists of a sulphonic acid. The light petroleum extract was evaporated to small bulk, when the oxazole crystallised. After recrystallisation from light petroleum it was obtained in hard, white nodules, melting at 83—84°. It is sparingly soluble in light petroleum, very soluble in chloroform, and less so but still quite readily soluble in alcohol, benzene, or ether. From the latter solvent it separates in slender prisms. The solutions are much more strongly fluorescent than those of the isomeric 5-phenyl-2-anisyloxazole:

0·1600 gave 0·4480 CO_2 and 0·0749 H_2O. C=76·4; H=5·2.
$C_{16}H_{13}O_2N$ requires C=76·5; H=5·2 per cent.

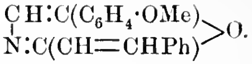
Minovici (*loc. cit.*) prepared a substance melting at 84—85° by the condensation of anisaldehyde and benzaldehydecyanohydrin, which is almost certainly identical with the above substance.

ω-*Cinnamoylamino*-p-*methoxyacetophenone*,
$MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH{:}CHPh$.

ω-Amino-*p*-methoxyacetophenone stannichloride (10 grams) dissolved in hot water (100 c.c.) and cooled to about 37° was mechanically stirred with molten cinnamoyl chloride (10 grams), and, when well mixed, treated with a cold aqueous solution of potassium hydroxide (30 grams in 30 c.c.). After two hours the solid was collected, dried, and crystallised from ether, in which it is sparingly soluble. The colourless prisms melt at 153—154°:

0·1495 gave 0·4010 CO_2 and 0·0785 H_2O. C=73·1; H=5·8.
$C_{18}H_{17}O_3N$ requires C=73·2; H=5·8 per cent.

5-*Anisyl-2-styryloxazole*,



$$\left.\begin{matrix}\mathrm{CH{:}C(C_6H_4{\cdot}OMe)} \\ | \\ \mathrm{N{:}C(CH{=}CHPh)}\end{matrix}\right>\mathrm{O}.$$

The preparation of this compound by the dehydration of the open-chain amide follows in all its details that of 2-phenyl-5-anisyloxazole (see p. 1305).

The substance crystallises from light petroleum in slender, radiating prisms, melting at 137°. It may also be crystallised from ether or even alcohol, and all its solutions exhibit intense blue fluorescence:

0·1393 gave 0·3972 CO_2 and 0·0708 H_2O. C = 77·8; H = 5·6.
$C_{18}H_{15}O_2N$ requires C = 77·9; H = 5·4 per cent.

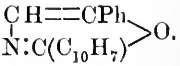
This compound should be identical with the substance which Minovici (*Ber.*, 1896, **29**, 2102) prepared by the condensation of anisaldehydecyanohydrin and cinnamaldehyde. Since, however, his product melted at 100°, it must have been a mixture.

ω-α-*Naphthoylaminoacetophenone*, $COPh{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}C_{10}H_7$.

ω-Aminoacetophenone stannichloride (40 grams) was dissolved in hot water (500 c.c.), and the solution cooled and treated with α-naphthoyl chloride (50 grams) and, with vigorous stirring, potassium hydroxide (150 grams) dissolved in its own weight of water. The red oil produced was extracted with much ether, and the ethereal solution washed many times with water. The ether distilled until the volume of the residue was about 100 c.c. The crystals which separated were recrystallised from methyl alcohol, when slender, colourless needles were obtained, melting sharply at 133°, and readily soluble in organic solvents with the exception of ether and light petroleum:

0·1210 gave 0·3497 CO_2 and 0·0580 H_2O. C = 78·8; H = 5·3.
$C_{19}H_{15}O_2N$ requires C = 78·9; H = 5·2 per cent.

5-*Phenyl-2-α-naphthyloxazole*,



$$\left.\begin{matrix}\mathrm{CH{=}CPh} \\ | \\ \mathrm{N{:}C(C_{10}H_7)}\end{matrix}\right>\mathrm{O}.$$

This brilliantly fluorescent oxazole derivative is very easy to recognise and purify, and we therefore investigated the action of various dehydrating agents on ω-naphthoylaminoacetophenone. It was found that acetic anhydride and acetyl chloride had no action, whilst the dehydration could be effected by means of phosphorus pentachloride, phosphoryl chloride, thionyl chloride, and best of all by sulphuric acid in the usual manner. The open-chain amide is incapable of existence in sulphuric acid solution, and on the addition of water the oxazole is obtained in practically pure condition and quantitative amount. It crystallises best from ethyl alcohol in pale yellow needles melting at 108°:

0·1241 gave 0·3844 CO_2 and 0·0563 H_2O. C = 84·5; H = 5·0.
$C_{19}H_{13}ON$ requires C = 84·1; H = 4·8 per cent.

It is readily soluble in benzene, chloroform, or ether, sparingly so in light petroleum or cold alcohol. All its solutions, including that in sulphuric acid, show intense bluish-violet fluorescence, which, when viewed in violet light, is phenomenal. Not only the solution but also the solid substance exhibits this striking property. The oxazole is a weak base, and does not readily form salts. It dissolves, however, in hot concentrated hydrochloric acid, and crystallises from solution as the hydrochloride, which forms plates with jagged edges, and is dissociated by water.

The *picrate*, produced by mixing a solution of the oxazole in methyl ethyl ketone with an alcoholic solution of picric acid, crystallises in yellow prisms melting at 160°.

α-Naphthyl iso*Nitrosomethyl Ketone*, $C_{10}H_7{\cdot}CO{\cdot}CH{:}N{\cdot}OH$.

α-Naphthyl methyl ketone (20 grams) was added to a solution of sodium ethoxide (2·6 grams Na) in alcohol (60 c.c.), and mixed with *iso*amyl nitrite (20 grams). The flask containing the mixture was closed, and cooled by a stream of water during twelve hours. The red sodium salt of the *iso*nitroso-compound was collected and dissolved in water, a certain amount of oil being removed by extraction with ether. The aqueous solution was cautiously acidified with acetic acid, when a milky liquid was produced, from which a solid substance gradually separated. This was collected and used for reduction in this form. A specimen was purified for analysis by crystallisation from chloroform. Colourless, satiny needles are so obtained, melting at 183°:

0·1074 gave 0·2848 CO_2 and 0·0465 H_2O. C = 72·3; H = 4·8.
$C_{12}H_9O_2N$ requires C = 72·4; H = 4·5 per cent.

The substance has the usual properties of an *iso*nitroso-ketone, and is readily soluble in most organic solvents.

α-Naphthyl Benzoylaminomethyl Ketone, $C_{10}H_7{\cdot}CO{\cdot}CH_2{\cdot}NHBz$.

α-Naphthyl *iso*nitrosomethyl ketone (10 grams) dissolved in a little alcohol was added, with cooling, to a solution of stannous chloride (32 grams) in concentrated hydrochloric acid (50 c.c.). The reduction is quickly finished, and, after half an hour, the pale yellow, crystalline deposit was collected and washed with concentrated hydrochloric acid. In order to identify the amine of which this substance is the stannichloride, a portion of the salt was dissolved in hot dilute hydrochloric acid, and hydrogen sulphide passed into the solution until it had a strong odour of the gas. The filtered liquid was boiled to expel the excess of hydrogen sulphide, and platinic chloride was then mixed with the warm solution. On cooling, the *platinichloride* of α-naphthyl aminomethyl ketone separated in pale orange needles, which melted and decomposed at 225—229°:

0·1638 gave 0·0408 Pt. Pt = 24·9.

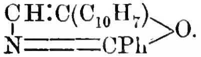
$(C_{12}H_{11}ON)_2,H_2PtCl_6$ requires Pt = 25·2 per cent.

For the benzoylation of the amine the stannichloride was employed, and the reaction was conducted in acid solution. α-Naphthyl aminomethyl ketone stannichloride (15 grams), suspended in a mixture of acetic acid (100 c.c.) and benzoyl chloride (25 grams), together with an excess of dry sodium acetate, was warmed on the water-bath for a quarter of an hour. The product was poured into water, the crystalline precipitate collected, and recrystallised from methyl alcohol. It forms slender, colourless needles, melting at 150°. The substance is readily soluble in benzene or chloroform, but sparingly so in alcohol, ether, or light petroleum:

0·1311 gave 0·3779 CO_2 and 0·0629 H_2O. C = 78·6; H = 5·3.

$C_{19}H_{15}O_2N$ requires C = 78·9; H = 5·2 per cent.

2-*Phenyl*-5-α-*naphthyloxazole*,



$$\left.\begin{matrix}CH{:}C(C_{10}H_7)\\ N{=\!=\!=\!=}CPh\end{matrix}\right>O.$$

α-Naphthyl benzoylaminomethyl ketone dissolves in sulphuric acid, yielding a yellow solution, which, however, quickly changes to a faint claret shade and acquires intense blue fluorescence. After three minutes the reaction is quite complete, and the oxazole may be precipitated by water. The solid was collected and extracted with hot alcohol, when a certain amount remained undissolved. After filtration the base was precipitated from its alcoholic solution by water, and was then recrystallised from methyl alcohol. The substance crystallises in flat needles melting at 116—117°. It has a scarcely perceptible yellow colour, and may for all practical purposes be called colourless. Its solutions, although fluorescent, do not exhibit the property in the marked manner which characterises the isomeric 5-phenyl-2-naphthyloxazole:

0·1033 gave 0·3188 CO_2 and 0·0441 H_2O. C = 84·2; H = 4·7.

$C_{19}H_{13}ON$ requires C = 84·1; H = 4·8 per cent.

The substance dissolves in concentrated hydrochloric acid, but in a short time the pale yellow, sparingly soluble hydrochloride crystallises from the solution.

The Picrate.—On mixing alcoholic solutions of the oxazole and picric acid, this derivative crystallises at once. After recrystallisation from alcohol the compound forms stout, yellow needles, melting at 142—144°.

ω-o-, -m-, *and* -p-*Nitrobenzoylaminoacetophenones*, $COPh{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$.

Ortho-compound.—A solution of ω-aminoacetophenone stannichloride (30 grams) in water (200 c.c.) was vigorously stirred mechanically with *o*-nitrobenzoyl chloride (40 grams). A 10 per cent. aqueous solution of sodium hydroxide was then added until the liquid was strongly alkaline and the precipitate at first formed had dissolved. When all the acid chloride had been decomposed, the aqueous layer was decanted, and the viscid, pale yellow residue became crystalline in contact with alcohol. The substance was collected and recrystallised from methyl alcohol, when colourless needles were obtained melting at 128°:

0·1274 gave 0·2972 CO_2 and 0·0514 H_2O. C=63·6; H=4·5.

$C_{15}H_{12}O_4N_2$ requires C=63·4; H=4·2 per cent.

Meta-compound.—This substance was prepared similarly to the preceding. The green, viscid mass resulting from the condensation was dissolved in methyl alcohol and allowed to crystallise, a process which, owing to the presence of impurities, is slow but ultimately almost complete. The compound was recrystallised from ethyl alcohol, and obtained in shining needles melting at 151°. It is sparingly soluble in the usual organic solvents:

0·1165 gave 0·2713 CO_2 and 0·0465 H_2O. C=63·5; H=4·4.

$C_{15}H_{12}O_4N_2$ requires C=63·4; H=4·2 per cent.

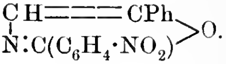
Para-compound.—Owing to the high melting point of *p*-nitrobenzoyl chloride it was found best to utilise in this case the process of acylation in acid solution devised by Gabriel (*loc. cit.*).

Sodium acetate (20 grams) was dissolved in acetic acid (50 c.c.), the solution cooled, and a finely powdered mixture of ω-aminoacetophenone stannichloride (10 grams) and *p*-nitrobenzoyl chloride (20 grams) added all at once. Heat was developed, and sodium chloride separated. After half an hour, during which time the flask was continually shaken, water and excess of dilute aqueous sodium hydroxide was added, and the solid collected. The washed precipitate was extracted with boiling alcohol, from which the substance crystallised in colourless needles. After recrystallisation it melts at 197°. In common with other *p*-nitro-derivatives, its solubility is smaller and its melting point higher than the same properties of the corresponding ortho- and meta-compounds:

0·1254 gave 0·2907 CO_2 and 0·0514 H_2O. C=63·2; H=4·6.

$C_{15}H_{12}O_4N_2$ requires C=63·4; H=4·2 per cent.

5-*Phenyl*-2-o-*nitrophenyloxazole*,



$$\begin{matrix}\mathrm{CH}{=\!=\!=\!=}\mathrm{CPh}\\ \mathrm{N}\colon\mathrm{C(C_6H_4\cdot NO_2)}\end{matrix}\!>\!\mathrm{O}.$$

ω-*o*-Nitrobenzoylaminoacetophenone (2 grams) was dissolved in sulphuric acid (10 c.c.) and gently warmed. After a quarter of an hour the bright yellow solution was diluted with water, and the oily precipitate extracted with benzene. The pale yellow extract was dried with potassium carbonate, and the solvent almost removed by distillation. Light petroleum (b. p. 50—60°) was then added until a cloudiness appeared, when, on allowing to remain in the ice-chest, the substance crystallised. After recrystallisation from methyl alcohol, in which it is sparingly soluble in the cold, the compound was obtained as well-defined and characteristic pale yellow, flat needles, melting at 118°:

0·1211 gave 0·3015 CO_2 and 0·0439 H_2O. C=67·9; H=4·0.

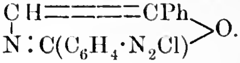
$C_{15}H_{10}O_3N_2$ requires C=67·7; H=3·8 per cent.

The solution of the oxazole in concentrated hydrochloric acid quickly deposits the hydrochloride as microscopic clusters of leafy crystals. This salt is dissociated by water, but is converted by platinic chloride and auric chloride into more stable brown, amorphous double salts.

5-*Phenyl*-2-o-*aminophenyloxazole and the Corresponding Diazonium Chloride*,

$$\begin{matrix}\mathrm{CH}{=\!=\!=\!=\!=}\mathrm{CPh}\\ \mathrm{N}\colon\mathrm{C(C_6H_4\cdot NH_2)}\end{matrix}\!>\!\mathrm{O}$$

and



$$\begin{matrix}\mathrm{CH}{=\!=\!=\!=\!=}\mathrm{CPh}\\ \mathrm{N}\colon\mathrm{C(C_6H_4\cdot N_2Cl)}\end{matrix}\!>\!\mathrm{O}.$$

5-Phenyl-2-*o*-nitrophenyloxazole (2 grams) was heated, for half an hour on the steam-bath, with granulated tin (5 grams) and concentrated hydrochloric acid (25 c.c.). A white, crystalline precipitate separated, consisting of a stannichloride. The liquid was diluted with water and extracted with ether, the ethereal solution washed, dried, and evaporated. The residue was then crystallised from dilute methyl alcohol, and so obtained as a crystalline, pale yellow crust, melting at 125°. The colour, although faint, appears to be characteristic of the substance, and was not removed by recrystallisations:

0·1014 gave 0·2832 CO_2 and 0·0493 H_2O. C=76·2; H=5·4.

$C_{15}H_{12}ON_2$ requires C=76·3; H=5·1 per cent.

The substance is readily soluble in all organic solvents, and its solutions have a bright blue fluorescence. It is a remarkably weak base in that, although it is a primary aromatic amine, its hydrochloride is dissociated in presence of much water. The base can, nevertheless, be readily diazotised by adding sodium nitrite to its suspension in dilute hydrochloric acid. The diazonium derivative so produced is characterised by its orange-yellow colour and great stability. Long-continued boiling of its aqueous solution is necessary to decompose it. The solid derivative is readily obtained by the addition of *iso*amyl nitrite to the solution of the base in ether containing hydrochloric acid. It is an orange, crystalline substance, melting and decomposing at 128°, and readily soluble in water. The diazo-compound gives an intense orange coloration with diethylaniline in neutral solution, which becomes crimson on the addition of hydrochloric acid. No combination, however, occurs in strongly acid solution. With β-naphthol and "R-salt" the coupling proceeds in faintly alkaline or weakly acid solution, but not at all in presence of excess of alkali hydroxide. The power to combine returns as the solution is acidified, so that this diazonium salt is evidently converted into an *iso*diazotate by potassium hydroxide. The azo-dye from "R-salt" is carmine, and exhibits in dilute aqueous solution a magnificent blue fluorescence, whilst that from β-naphthol is rich crimson.

The diazonium chloride forms double salts even more stable than the parent substance. The *aurichloride* is an orange-red powder, which melts and explodes at 163°. Great difficulty was experienced in its analysis, which was, however, accomplished by decomposing successive small quantities from a weighing tube in a crucible containing some sand:

0·1021 gave 0·0335 Au. Au = 32·8.

$C_{15}H_{10}ON_3,AuCl_4$ requires Au = 33·6 per cent.

The *platinichloride* is very sparingly soluble, and is produced as a crystalline, orange-yellow precipitate when platinic chloride is added to an aqueous solution of the diazonium chloride.

5-*Phenyl*-2-m-*nitrophenyloxazole.*

The method employed for the preparation of this substance is identical with that used for the *o*-nitro-isomeride up to the stage of pouring the solution in sulphuric acid into water, when in this case the oxazole is obtained at once in the crystalline condition, and may be recrystallised from methyl or ethyl alcohols, solvents in which the compound is sparingly soluble in the cold.

5-*Phenyl*-2-m-*nitrophenyloxazole* forms light yellow needles melting at 149°. The melting point of a mixture of the substance and the straight-chain amide, which melts at 151°, was 130—134°:

0·2013 gave 0·4982 CO_2 and 0·0729 H_2O. C=67·5; H=4·0.

$C_{15}H_{10}O_3N_2$ requires C=67·7; H=3·8 per cent.

The substance dissolves slowly in concentrated hydrochloric acid, and, on keeping, the hydrochloride of the base separates as microscopic prisms of very definite shape. A small quantity of the nitro-compound was boiled with tin and hydrochloric acid until the colourless precipitate first formed passes into solution. On dilution this liquid gives no precipitate, and nothing can be extracted by means of ether. 5-Phenyl-2-*m*-aminophenyloxazole is therefore a base which forms a hydrochloride stable in aqueous solution, and thus differs from the corresponding *o*-compound. The solution was rendered strongly alkaline, and ether now extracted a substance which imparted intense violet fluorescence to the extract. This fluorescence was removed by shaking with dilute hydrochloric acid, which consequently dissolved the amine. On the addition of sodium nitrite, the colourless acid solution became orange-yellow, and now contained a diazonium salt, the properties of which are very similar to those of the substance already described. It is stable, coloured, readily changed into an *iso*diazotate, and yields with β-naphthol and sodium acetate a crimson azo-compound. The orange-yellow compound, produced on combination with dimethylaniline, is very sensitive to mineral acid, becoming crimson in presence of a slight excess of hydrochloric or sulphuric acids.

5-*Phenyl*-2-p-*nitrophenyloxazole.*

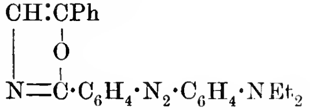
When ω-*p*-nitrobenzoylaminoacetophenone (1 gram) was dissolved in sulphuric acid (10 c.c.) a colourless solution was at first produced, but this rapidly became yellow, and after remaining at the room temperature for an hour, water was added, and the bright yellow precipitate collected. The substance is remarkably sparingly soluble in many solvents which dissolve the ortho- and meta-derivatives with ease; thus it is only sparingly soluble in boiling ethyl alcohol, and crystallises completely from the solution, on cooling, in minute, rectangular plates of characteristic appearance. It is best crystallised from ethyl acetate, and so obtained in bright yellow leaflets melting at 202—204°:

0·1184 gave 0·2923 CO_2 and 0·0404 H_2O. C=67·3; H=3·8.

$C_{15}H_{10}O_3N_2$ requires C=67·7; H=3·8 per cent.

Minovici (*Ber.*, 1896, **29**, 2106) has shown that the nitration of 2:5-diphenyloxazole yields a mononitrodiphenyloxazole which has the nitro-group in the para-position, since *p*-nitrobenzoic acid was obtained from it by oxidation with chromic acid. We have prepared this substance, and find that it is quite different from the 5-phenyl-2-*p*-nitrophenyloxazole produced as described above. It is more soluble, and crystallises from both ethyl acetate and alcohol in woolly needles melting at 189—190°. The melting point was depressed 20° by admixture of the substance with an equal quantity of 5-phenyl-2-*p*-nitrophenyloxazole. It follows that the product of nitration of 2:5-diphenyloxazole is 5-*p*-nitrophenyl-2-phenyloxazole. These two bright yellow *p*-nitrodiphenyloxazoles have the curious property of yielding solutions which are very nearly colourless. This fact, combined with their sparing solubility and high melting points, indicates a difference of molecular complexity of the substances in the solid state and in solution.

5-Phenyloxazole-2-p-*benzeneazodiethylaniline*,



$$\begin{array}{l} \mathrm{CH{:}CPh} \\ |\qquad\;\; | \\ |\qquad\;\; \mathrm{O} \\ |\qquad\;\; | \\ \mathrm{N{=}C\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NEt_2} \end{array} .$$

5-Phenyl-2-*p*-nitrophenyloxazole was reduced by means of an excess of tin and hydrochloric acid at 100° in half an hour. The product was rendered strongly alkaline, and the base extracted with ether. *5-Phenyl*-2-p-*aminophenyloxazole* forms a crystalline cake when the ether is evaporated nearly to dryness. It melts at 188—189°, and imparts an intense violet-blue fluorescence to its solutions. It is readily diazotised in dilute hydrochloric acid solution, yielding an orange-yellow diazonium chloride, which crystallises from the aqueous solution in needles. The substance may with care be recrystallised from water. It melts at 153—155° without decomposition, which, however, occurs at a higher temperature or at the melting point if the capillary tube is not quickly cooled. The fused and re-solidified diazonium chloride will still combine with β-naphthol, yielding a crimson azo-compound.

This diazonium salt is therefore of great stability, and it requires prolonged boiling with water in order to decompose it. The product of this decomposition is a colourless phenol, which crystallises in needles, is sparingly soluble, and melts at 240—250°. It dissolves in alkali hydroxides, yielding colourless solutions having intense blue fluorescence, and is almost certainly *5-phenyl*-2-p-*hydroxyphenyloxazole*.

The diazonium chloride can be changed into an *iso*diazotate by dissolving in concentrated aqueous potassium hydroxide. The potassium compound separates as a crystalline powder, and the addition of β-naphthol to the liquid causes only a faint red colour.

The compound obtained by combining the diazonium chloride with diethylaniline is best produced by dissolving the salt in alcohol and adding a slight excess of the base. The *azo*-compound crystallises from the solution, and after recrystallisation from alcohol is obtained in orange leaflets melting at 155°:

0·1062 gave 0·2964 CO_2 and 0·0594 H_2O. C=76·1; H=6·2.

$C_{23}H_{24}ON_4$ requires C=75·8; H=6·1 per cent.

The substance is readily soluble in hot alcohol. It gives a crimson solution in hydrochloric acid.

α-*Benzoylaminopropiophenone*, COPh·CHMe·NHBz.

Aminopropiophenone stannichloride (15 grams) (Behr-Bregowski, *Ber.*, 1897, **30**, 1521) was suspended in water (150 c.c.), cooled with ice, and treated with benzoyl chloride (10 grams) and aqueous potassium hydroxide (45 grams in 75 c.c.), the liquid being mechanically stirred. When all the acid chloride had been decomposed, the product was extracted with ether, and the ethereal solution evaporated to small bulk. The crystals which separated were recrystallised from ether, in which the pure substance is sparingly soluble, and the colourless prisms so obtained melted at 104—105°. The substance is readily soluble in benzene or chloroform, and sparingly so in ether or light petroleum:

0·1688 gave 0·4672 CO_2 and 0·0940 H_2O. C=75·5; H=6·2.

0·2893 ,, 13·8 c.c. N_2 at 18° and 762 mm. N=5·6.

$C_{16}H_{15}O_2N$ requires C=75·8; H=5·9; N=5·5 per cent.

This amide was readily changed into the oxazole described in the next section, but the reaction was less successful in the case of two other acylated aminopropiophenones, namely, the *o*-toluoyl and cinnamoyl compounds.

α-o-*Toluoylaminopropiophenone* was prepared similarly to the benzoyl derivative, and after crystallisation from ether melted at 99—100°:

0·2195 gave 9·4 c.c. N_2 at 21° and 764 mm. N=5·0.

$C_{17}H_{17}O_2N$ requires N=5·2 per cent.

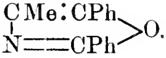
α-*Cinnamoylaminopropiophenone*, obtained by the usual method, crystallises from ether in prisms melting at 125°. It is very soluble in benzene:

0·2100 gave 0·5929 CO_2 and 0·1130 H_2O. C=77·0; H=5·9.

$C_{18}H_{17}O_2N$ requires C=77·4; H=6·1 per cent.

When these two substances were treated with sulphuric acid, fluorescent solutions were obtained, but no satisfactory crystalline material could be isolated from the solution. This is very possibly due to sulphonation.

2:5-*Diphenyl-4-methyloxazole*,



$$\left.\begin{array}{l}\mathrm{CMe{:}CPh}\\ \mathrm{N{=\!=}CPh}\end{array}\right>\mathrm{O}.$$

α-Benzoylaminopropiophenone dissolves readily in sulphuric acid, and the solution, when diluted with water, furnishes a crystalline precipitate of the oxazole derivative. The substance is best crystallised from light petroleum, in which it is sparingly soluble in the cold, and from which it separates in flat, monoclinic prisms, melting at 82°. It dissolves readily in most organic solvents, yielding fluorescent solutions:

0·1607 gave 0·4808 CO_2 and 0·0800 H_2O. C=81·6; H=5·5.

$C_{16}H_{13}ON$ requires C=81·7; H=5·5 per cent.

THE UNIVERSITY, MANCHESTER.

CXL.—*The Absorption Spectra of Various Derivatives of Naphthalene in Solution and as Vapours.*

By JOHN EDWARD PURVIS.

THE author has already given accounts (Trans., 1910, **97**, 692, 1035, 1546; 1911, **99**, 811, 1699, 2318) of the absorption spectra of various alkyl and halogen derivatives of benzene and other substances under different physical conditions.

The absorption spectra of naphthalene has been described by Hartley (Trans., 1885, **47**, 685) and by Baly and Tuck (Trans., 1908, **93**, 1902), and the latter authors have also compared the absorption spectra of acenaphthene, acenaphthalene, α-tetrahydronaphthalene, etc., with that of naphthalene (*loc. cit.*).

The aim of this investigation is to give an account of the absorption spectra, in the more refrangible regions, of solutions of various derivatives of naphthalene; and also a comparison of several of them when in the vaporous condition. The following substances were examined: Naphthalene, α- and β-chloronaphthalenes, α- and β-bromonaphthalenes, α- and β-naphthols, α- and β-naphthaquinones, α- and β-naphthylamines, α- and β-nitronaphthalenes, α-nitro-β-naphthylamine, acenaphthene, and 4-chloro-, 4-bromo-, and 4-iodo-acenaphthenes. The vapours of naphthalene, tetrahydronaphthalene, α- and β-chloronaphthalenes, and α- and β-bromonaphthalenes were examined.

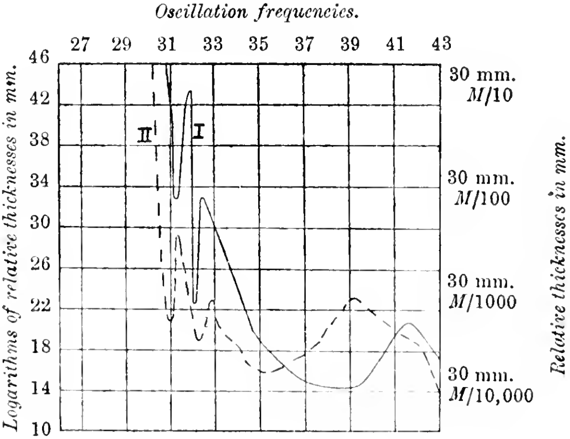
Each substance was dissolved in absolute alcohol beginning with *M*/10-strength, and diluting to *M*/10,000-strength. The two naphthaquinones were dissolved in chloroform. The method of observation has been described before by the author (*loc. cit.*). The source of light was the condensed cadmium spark, and also the condensed molybdenum-uranium spark, in order to study regions of the spectrum which are covered up by several of the strong cadmium lines. The photographs were taken and the curves plotted in the usual way.

Description of Absorption Curves.

Solutions.

Naphthalene and Acenaphthene.—In order to compare the compounds of the two substances, the author has repeated the observations of Baly and Tuck, and drawn the curves (Fig. 1) from photographs taken under similar conditions. The acenaphthene curve differs a little from that described by Baly and Tuck, in that there is a weak band at about 3230, and a very weak, doubtful indication of another between 3320 and 3380.

Fig. 1.

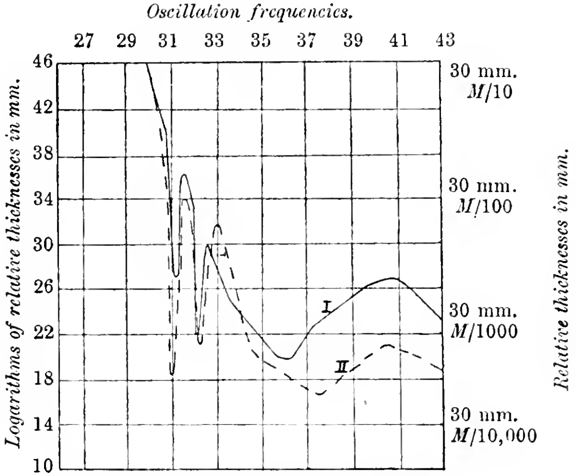


I (continuous line): *Naphthalene.*
II (dotted line): *Acenaphthene.*

α- and β-Chloronaphthalenes.—The general form of the curves (Fig. 2) is similar to the naphthalene curve. Compared with each other, the chief differences are that the two less refrangible bands of the α-compound are narrower and not so persistent as the corresponding bands of the β-compound; and the large most refrangible band of the β-compound is wider and less persistent than that of the α-compound.

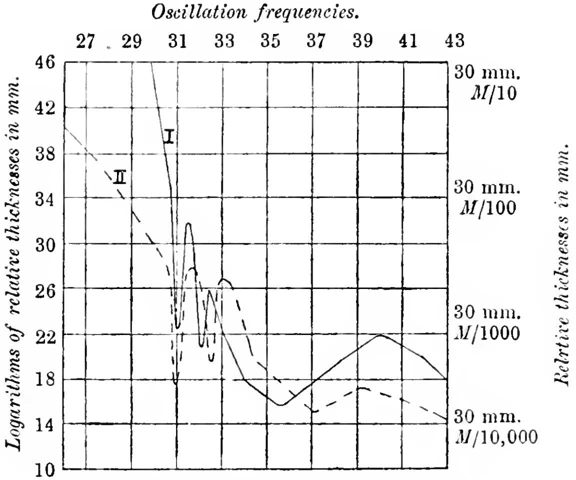
α- and β-Bromonaphthalenes.—A comparison (Fig. 3) extends to those compounds like that of the two chloronaphthalenes. It may

Fig. 2.



I (continuous line): *α-Chloronaphthalene.*
II (dotted line): *β-Chloronaphthalene.*

Fig. 3.



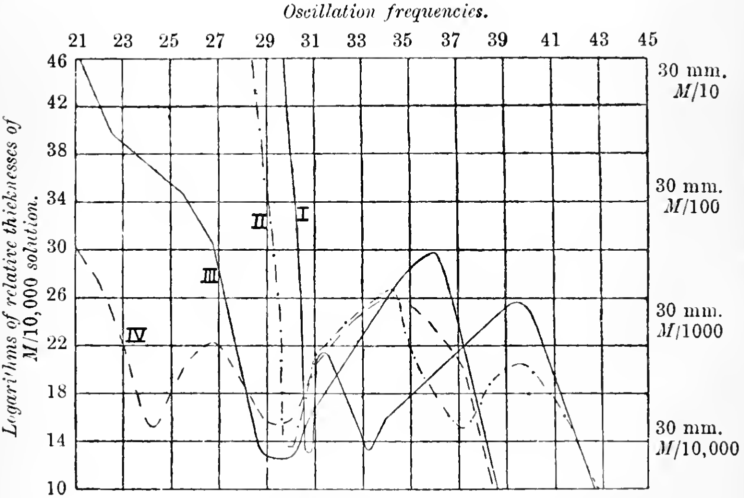
I (continuous line): *α-Bromonaphthalene.*
II (dotted line): *β-Bromonaphthalene.*

also be noted that the general absorption of the β-compound rapidly extends to the less refrangible regions; and in the strongest solutions there is a band in the visible regions connected with the red colour.

α- and β-Naphthols.—Both compounds show two bands (Fig. 4, I and II). There is a general resemblance to the two more refrangible bands of naphthalene, and compared with each other the bands are widened out in the β-compound; the phenomena are not unlike those of the halogen derivatives in this respect.

α- and β-Naphthaquinones.—There are striking differences in these two compounds (Fig. 4, III and IV). The α-compound has one large band, whereas the β-compound has two; the less refrangible one is in the visible regions, and the more refrangible one is comparable in position with the band of the α-compound, but it is not so strong. It is also to be noted that there is a rapid extension of the general absorption towards the red end which is connected with the colour of these compounds.

FIG. 4.

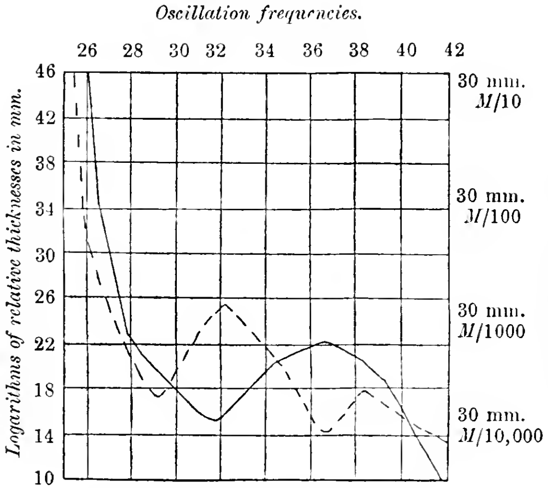


I. α-*Naphthol.*
II. β-*Naphthol* (dot and dash line).
III. α-*Naphthaquinone.*
IV. β-*Naphthaquinone* (dash line).

α- and β-Naphthylamines.—The α-compound exhibits one large band (Fig. 5), and in the β-compound there are two bands, the more refrangible one being very weak.

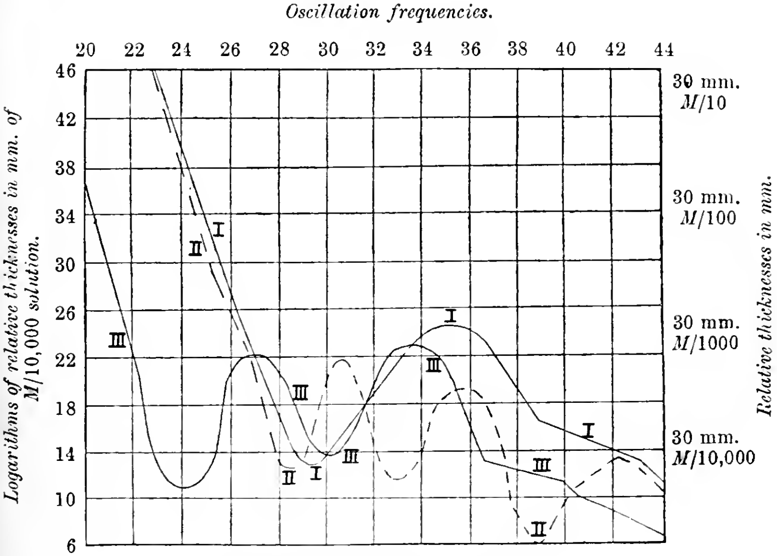
α- and β-Naphthylamines and Hydrochloric Acid.—In one series of observations, 0·5 equivalent of hydrochloric acid was added to the two solutions; and a slight excess of hydrochloric acid was used in

FIG. 5.



I (continuous line): *a-Naphthylamine.*
II (dotted line): *β-Naphthylamine.*

FIG. 6.

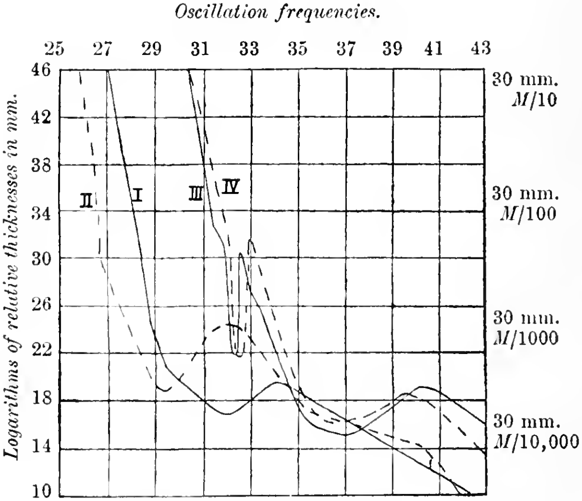


I. *a-Nitronaphthalene.*
II. *β-Nitronaphthalene* (dotted line).
III. *a-Nitro-β-naphthylamine.*

another series. It will be seen (Fig. 6) that, in the 0·5 equivalent solutions, the bands are not unlike those of the bases themselves, but they are very much reduced; whereas when excess of hydrochloric acid was added the bands are not unlike the two more refrangible bands of naphthalene, except that they are not so strong; and this is especially noticeable in the large most refrangible band at 3700.

α- and β-Nitronaphthalenes.—There is one very large band at 2950 in the α-compound (Fig. 7), and a weak one indicated by the rapid extension of the line between 3890 and 4300. In the β-compound there are two bands at 2820 and 3300 taking the place of the α-band at 2950; and a weak band in the more refrangible side at 3900, corresponding with the weak band of the α-compound between 3890 and 4300. The general absorption in both compounds is also rapidly extended towards the edge of the visible regions of the spectrum.

FIG. 7.

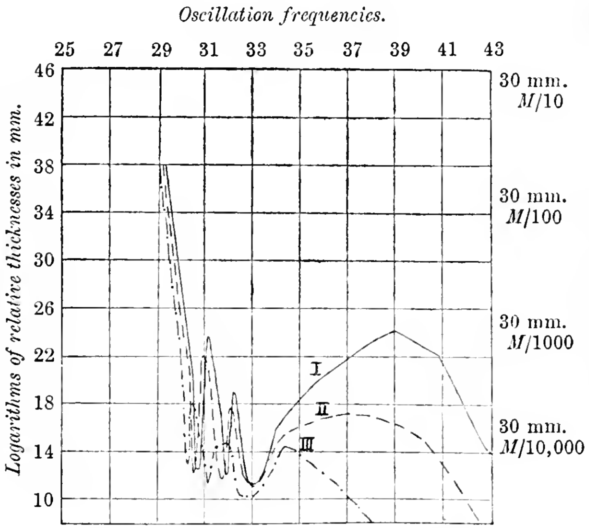


I. α-*Naphthylamine* + ½ *eq.* HCl.
II. β *Naphthylamine* + ½ *eq.* HCl.
III. α-*Naphthylamine* + *excess* HCl.
IV. β-*Naphthylamine* + *excess* HCl.

α-Nitro-β-naphthylamine (Fig. 7).—There are two well-marked bands at 2400 and 3000, and a very weak indication of a band between 3650 and 4000, which corresponds with the large most refrangible band of naphthalene. The band at 2400 is well within the visible spectrum, and is connected with the colour of the compound. There is a fair comparison of the curve with that of β-nitronaphthalene on the one hand, and that of β-naphthylamine on the other, the chief difference being the marked weakening of the most refrangible band—a naphthalene band—and, of course, a difference in position.

In two other series of experiments both 0·5 equivalent hydrochloric acid and slight excess of hydrochloric acid were added to this substance, but their absorption curves were very similar to that of the original substance, indicating that, unlike the naphthylamines, the addition of acid has no apparent effect on the vibrations.

Fig. 8.



I (continuous line): 4-*Chloroacenaphthene.*
II (broken line): 4-*Bromoacenaphthene.*
III (dot and dash line): 4-*Iodoacenaphthene.*

4-Chloroacenaphthene, 4-Bromoacenaphthene, and 4-Iodoacenaphthene.—It will be seen (Fig. 8) that the bands have a general similarity to those of acenaphthene, but there are important differences to be noted. In the first place, the bands are a little nearer together in the three halogen compounds than in the acenaphthene, and the two least refrangible bands of the chlorine compound are wider and more persistent than the corresponding bromine and iodine compounds. The bands of the iodine compound are exceedingly narrow and have small persistency, and the large most refrangible band is very much reduced.

Vapours.

The author has already described the absorption spectra of the vapours of various benzene compounds (*loc. cit.*). The vapours of naphthalene, of the α- and β-chloro- and bromo-derivatives of naphthalene, and of acenaphthene have now been investigated. The liquids did not present much difficulty, and the apparatus used in the earlier experiments was sufficient for the purpose. A special form of apparatus, however, was used for the solids. It consisted of a small silica cell of about 5 mm. internal diameter with two clear windows opposite to each other, and with a small exit tube to connect with a pump. The cell was fitted in an iron receptacle lined with asbestos, and in which were two openings opposite the two windows of the silica cell. Two thermometers were fixed in close connexion with the cell, to observe the temperature of that neighbourhood. The temperatures mentioned below do not, therefore, represent the temperatures inside the cell, which would be a little lower than just outside, but it could not differ by more than a few degrees. A little of each substance was placed in the cell, which was then connected with a Töpler pump and exhausted. A clamp isolated the cell from the rest of the pump when the exhaustion was completed. The cell was introduced into the asbestos-lined box and the temperature raised; photographs were taken at successively increased temperatures. No attempt was made to measure the pressure of the vapour, as the aim of the experiments was a qualitative one.

It will be remembered that the vapours of benzene and of several of its chloro- and bromo-derivatives (*loc. cit.*) exhibit a large number of absorption bands which are wholly different from both the solution bands and the thin films; and that in the case of the iodo-derivatives of benzene the bands completely disappear (*loc. cit.*). The vapours of naphthalene and of several of its compounds, as described below, do not exhibit a series of bands like benzene. In naphthalene vapour there is no evidence of the large number of narrow bands so characteristic of benzene; in fact, the bands are diffuse wide bands very like those of the solution bands, and they are comparable with them except in position. The following notes describe the phenomena.

Naphthalene.

t°.	
100°	The rays were absorbed between λ 2700 and λ 2540, and then transmitted to about λ 2270. This large band corresponds with the large most refrangible band of the solution of naphthalene (Fig. 1).

Naphthalene (continued).

t°.	
120	The rays were absorbed between λ 2770 and λ 2420, and then transmitted to λ 2300. The rays were also weak between λ 3120 and λ 3095. The former band again corresponds with the large most refrangible naphthalene solution band; the latter with the narrow naphthalene solution band at 3210 (oscillation frequencies, Fig. 1).
140	The rays were absorbed from λ 2830, and they were weak between λ 3130 and λ 3090; the latter again corresponds with the naphthalene solution band at 3210, and becomes wider at the increased temperature and pressure.
160	The rays were absorbed from λ 2850, and they were weak between λ 3130 and λ 3085.
180	There was a well-marked band between λ 3130 and λ 3100; the rays were weak between λ 3240 and λ 3190, and there was general absorption from λ 3080. That is to say, the bands between λ 3240 and λ 3190 and between λ 3130 and λ 3100 correspond with the two narrow refrangible solution bands at 3130 and 3210 (oscillation frequencies).

a-Chloronaphthalene.

t°.	Pressure in mm.	
45°	830	The rays were transmitted to λ 2270.
60	860	The rays were absorbed between λ 2780 and λ 2490, and then transmitted to λ 2270. That is to say, the band between λ 2780 and λ 2490 corresponds with the strong solution band at 3600 (oscillation frequencies, Fig. 2).
75	890	The rays were absorbed from λ 2850.
90	920	,, ,, ,, ,, λ 2930.

There was not sufficient vapour in the tube to bring out the two narrow less refrangible bands corresponding to the solution bands.

β-Chloronaphthalene.—After the exhaustion, the pressure at the temperature of the laboratory indicated by the gauge was 5 mm.

t°.	
110°	The rays were absorbed from λ 2330.
120	,, ,, ,, ,, λ 2330.
130	,, ,, ,, between λ 2650 and λ 2430, and then transmitted to λ 2360.
140	The rays were absorbed between λ 2770 and λ 2420, and then transmitted to λ 2380. That is to say, the band between λ 2770 and λ 2420 corresponds with the large solution band at 3750 (oscillation frequeneies, Fig. 3).
160	The rays were absorbed from λ 2860.
180	The rays were weak between λ 3250 and λ 3200 and between λ 3100 and λ 3050, and they were totally absorbed from λ 2880.
200	The rays were weak between λ 3260 and λ 3200 and between λ 3100 and λ 3060, and they were totally absorbed from λ 2920.
220	The rays were absorbed between λ 3260 and λ 3190 and between λ 3130 and λ 3050, and they were totally absorbed from λ 2960. That is to say, the vapour band between λ 3260 and λ 3190 corresponds with the solution band at 3090 (oscillation frequencies), and that between λ 3130 and λ 3050 corresponds with the solution band at 3220 (oscillation frequencies, Fig. 2).

α-Bromonaphthalene.

t°.	Pressure in mm.	
60°	860	The rays were transmitted to λ 2270.
75	890	The rays were absorbed between λ 2810 and λ 2500, and then transmitted to λ 2300. That is to say, the vapour band between λ 2810 and λ 2500 corresponds with the strong solution band at 3550 (Fig. 3).
90	920	The rays were totally absorbed from λ 2920.

There was not sufficient vapour in the tube to bring out the narrow less refrangible bands corresponding with the solution bands.

β-Bromonaphthalene.—After the exhaustion the pressure indicated by the gauge was 14 mm. at the temperature of the room.

t°.	
100°	The rays were transmitted to about λ 2320.
120	The rays were weak between λ 2740 and λ 2420, and then transmitted to λ 2360.
140	The rays were very weak between λ 2740 and λ 2420, and then transmitted to λ 2400. That is to say, the band between λ 2740 and λ 2420 corresponds with the large solution band at 3720 (Fig. 3).
160	The rays were absorbed from λ 2800.
200	The rays were weak between λ 3270 and λ 3100, very weak between λ 3070 and λ 3050, and they were totally absorbed from λ 2880.
220	The rays were absorbed between λ 3260 and λ 3100 and between λ 3090 and λ 3040, and they were completely absorbed from λ 2630. That is to say, the bands between λ 3260 and λ 3100 and between λ 3090 and λ 3040 correspond respectively with the solution bands at 3100 and 3260 (oscillation frequencies, Fig. 3).

Acenaphthene.

t°.	Pressure in mm.	
75°	890	The rays were weak between λ 3205 and λ 3190 and between λ 3060 and λ 3040, and then transmitted to λ 2290.
80	912	The rays were weak between λ 3210 and λ 3190 and very weak between λ 3060 and λ 3040, and very weak between λ 2800 and λ 2700.
85	925	The rays were almost completely absorbed between λ 3220 and λ 3190 and between λ 3060 and λ 3040, and there was complete absorption between λ 2800 and λ 2690 ; they were then transmitted to λ 2390. The rays were very weak between λ 2970 and λ 2940 also.
90	936	The rays were absorbed between λ 3220 and λ 3190 and between λ 3070 and λ 3035, and then transmitted to λ 2380 ; they were also very weak between λ 2930 and λ 2550, but the indications were not very clear. That is to say, there are three well-marked bands in the vapour of acenaphthene, which correspond in appearance with the solution bands. They are comparable with the solution bands at 3090, 3220, and 3530 (oscillation frequencies, Fig. 1).

Tetrahydronaphthalene.

$t°$.	Pressure in in mm.	
15°	763	The rays were transmitted to λ 2210.
30	803	The rays were absorbed between about λ 2600 and λ 2400, and then transmitted to λ 2260.
45	833	The rays were transmitted to λ 2700.
60	863	The rays were transmitted to λ 2760.
75	893	The rays were transmitted to λ 2840.
90	923	The rays were transmitted to λ 2930. That is to say, there is one large band in the vapour of tetrahydronaphthalene which corresponds with the solution band found by Baly and Tuck (*loc. cit.*), the head of which is at about 3960 (oscillation frequencies).

The general results of the vapours are that (1) the vapours of naphthalene and of several of its derivatives exhibit absorption bands comparable in number and in appearance with the solution bands of the substances, and differing only slightly in position; and (2) as the temperature and pressure increase the stronger bands become wider, the weaker bands make their appearance and become stronger, and the general absorption is shifted towards the less refrangible regions.

Discussion of Results.

The chief results of this investigation are that the nature and type of the solution bands of various derivatives of naphthalene are controlled by the nature and type of the substituting atom or group of atoms; and that the vapour of some of these substances show absorption bands which are comparable with the solution bands. The differences in the curves of the α- and β-compounds are clearly marked in all the substances; and the alteration of the vibrations is very noticeable when the introduced radicle is in the β-position. By introducing the radicle in the β-position, the tendency is to dislocate the vibrations, so that wider bands are produced, as in the halogen derivatives and the naphthols; and also to break up the large bands into two as in the naphthaquinones, the naphthylamines, and the nitronaphthalenes.

In benzene and its derivatives (*loc. cit.*) the author has suggested that differences in the nature and type of the absorption bands, produced by the oscillatory vibration of the ring, is influenced by the nature and type of the substituting atom or groups of atoms, by their orientation, and by the physical conditions of the vibrating system. The suggestion may be applied to explain the differences in the absorption spectra of naphthalene and its derivatives. The naphthalene molecule may be considered to possess rhythmical oscillations, and these oscillatory movements are influenced by the kind of introduced atom or atomic groups, and also by their relative positions. The halogen compounds and the naphthols do not show widely marked differences from the original naphthalene; whereas in the nitronaphthalenes, the quinones, and the amines there are well-marked differences. These differences may be considered to be alterations in the oscillatory movements of the original molecule, whereby the various bands are widened. It may be mentioned that Hartley, Dobbie, and Lauder (Trans., 1902, **81**, 929) found only one band in phenol, whereas benzene has seven bands; and two large bands were found in *p*-benzoquinone. Baly and Collie (Trans., 1905, **87**, 1344) noticed a rapid extension of the rays between 3890 and 4200 in nitrobenzene, which is an undoubted weak band; and there is also a similar great absorptive power to that of the nitronaphthalenes, as is evident by the rapid extension of the line of general absorption towards the red end.

Nevertheless, there can be little doubt that the free valencies of various atoms exercise a considerable influence on the vibrations; for example, the two naphthylamines exhibit large bands; but when the bases are partly neutralised by 0·5 equivalent hydrochloric acid, the bands are considerably reduced, and when they are wholly neutralised the alteration in the character of the bands is very marked; the most refrangible naphthalene band just makes its appearance. On the other hand, no change was observed when the acid was added to α-nitro-β-naphthylamine; and the explanation appears to be that the free valencies of the nitro- and the amino-groups neutralise each other, and the characteristic vibrations are unaltered.

The author may recall the observations of the absorption spectra of various iodo-derivatives of benzene and toluene (Trans., 1911, **99**, 2318), which show that in the ultraviolet regions there was no selective absorption in the alcoholic solutions or in the vapours or in the thin films. It will be noticed that of the absorption bands of the halogen derivatives of acenaphthene (Fig. 10), those of 4-iodoacenaphthene are exceedingly weak; in fact, in the original photographs the bands are only just visible. The phenomena are not at all unlike those of the iodine derivatives of benzene, and the explanation may be the same. The iodine atom does not, however, destroy the oscillatory vibrations of the acenaphthene; it does not wholly damp and dislocate its movements, but it reduces them very considerably, so that the bands are very weak, but they are not eliminated.

This persistent stability of the oscillations of the naphthalene molecule is also suggested by the fact that the vapours of naphthalene, acenaphthene, tetrahydronaphthalene, and the isomeric α- and β-chloro- and bromo-naphthalenes exhibit absorption bands which are not unlike those of the solution bands. The conclusion seems to be that the oscillations of the naphthalene nuclei, as vapours, are more constrained than those of the benzene nucleus, the vapour of which shows a large number of bands. The vapours of naphthalene and its derivatives have not the same freedom of movement, and consequently their power of selective absorption is more like that of the solutions. The two conjugated nuclei of the naphthalene molecule damp the freer oscillations of the single benzene nucleus, even when the substance is in the state of vapour. The intrinsic vibratory energy is not altered, either by the freer movements or by the mutual bombardments of the rapidly moving molecules, and the stability of the vibrations is retained under both physical conditions.

I desire to thank the Government Grant Committee of the Royal Society, by whose assistance the apparatus used in this research was partly defrayed; and also Professor Pope for the three halogen derivatives of acenaphthene.

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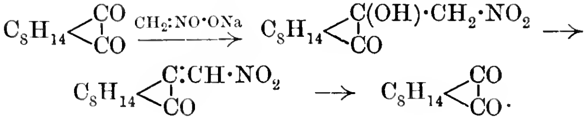
Cambridge.

CXLI.—*Studies in the Camphane Series. Part XXXI. Condensation of Camphorquinone with Nitromethane, Ethyl Cyanoacetate, and Phenylacetonitrile.*

By Martin Onslow Forster and John Charles Withers.

The facility with which camphorquinone undergoes condensation with typical substituted ammonia derivatives, such as hydroxylamine, hydrazine, semicarbazide, phenylhydrazine, and aniline, suggested the possibility that the other great class of changes to which carbonylic substances are prone, namely, condensation with suitable derivatives of methane, might be brought about between camphorquinone and, for example, nitromethane, ethyl cyanoacetate, phenylacetonitrile, acetophenone, and dinitrotoluene. The products would be derivatives of methylenecamphor, a class comprising hydroxymethylenecamphor, benzylidenecamphor, camphoroxalic acid, and enolic benzoylcamphor, presenting features, stereochemical and otherwise, which render more complete study of the group desirable.

In a restricted degree the above anticipation has been realised. Camphorquinone undergoes condensation with nitromethane very readily, and the resulting nitromethylenecamphor is accompanied, under certain conditions, by the intermediate nitromethylhydroxycamphor; nitromethylenecamphor is not mutarotatory in organic media, but the solution in aqueous sodium hydroxide, although colourless when cold, rapidly yields camphorquinone if heated:

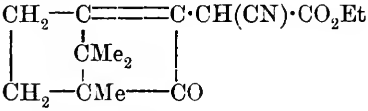


$$C_8H_{14}<\begin{array}{l}CO\\|\\CO\end{array} \xrightarrow{CH_2{:}NO{\cdot}ONa} C_8H_{14}<\begin{array}{l}C(OH){\cdot}CH_2{\cdot}NO_2\\|\\CO\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}CH{\cdot}NO_2\\|\\CO\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CO\\|\\CO\end{array}.$$

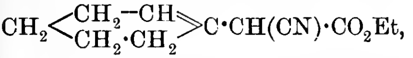
On mixing camphorquinone with ethyl cyanoacetate in alcohol containing a small proportion of sodium ethoxide, the liquid becomes warm, and soon deposits brilliant, sulphur-yellow crystals. Ethyl camphorylidenecyanoacetate, $C_8H_{14}<\begin{array}{l}C{:}C(CN){\cdot}CO_2{\cdot}C_2H_5\\|\\CO\end{array}$, as the substance may be called, is converted by ammonia into the amide, but with excess of alcoholic alkali is transformed into a dark brown, tarry material, accompanied by liberation of ammonia; only when a single molecular proportion of sodium ethoxide is employed does hydrolysis lead to camphorylidenecyanoacetic acid, and the corresponding camphorylidenemalonic acid, $C_8H_{14}<\begin{array}{l}C{:}C(CO_2H)_2\\|\\CO\end{array}$, can be obtained by heating the substituted cyanoacetic acid with hydrobromic acid in a sealed tube.

A series of derivatives parallel with those from cyanoacetic ester has been produced also by using phenylacetonitrile; the initial condensation proceeds even more readily with this substance, the resulting phenylcyanomethylenecamphor, $C_8H_{14}<\begin{array}{l}C{:}C(CN){\cdot}C_6H_5\\|\\CO\end{array}$, being bright yellow, and having $[\alpha]_D$ 246°, whence $[M]_D$ 652°. It is interesting to compare this substance with benzylidenecamphor, of which it is the cyano-derivative, and which has $[M]_D$ 1020°; thus, contrary to expectation, the cyano-group, although highly unsaturated, fails to enhance the activity of the molecule into which it enters, and in this respect resembles the hydroxy-group, since enolic benzoylcamphor has $[M]_D$ 720°. The behaviour of phenylcyanomethylenecamphor is distinct from that of camphorylidenecyanoacetic acid and its ester towards alkalis, which readily transform it into the amide, whence the acid, camphorylidenephenylacetic acid, $C_8H_{14}<\begin{array}{l}C{:}C(C_6H_5){\cdot}CO_2H\\|\\CO\end{array}$, is obtainable by the action of nitrous acid.

In reviewing these products it is necessary to point out that the various constitutional formulæ given above must not be assumed without definite evidence, because the experiments of Haworth (Trans., 1909, **95**, 480; compare also Gardner and Haworth, *loc. cit.*, 1955, likewise Harding and Haworth, Trans., 1910, **97**, 486) have revealed the possibility of an alternative course, according to which the product of condensing camphorquinone with ethyl cyanoacetate, for instance, would have the constitution:



Haworth found that when condensation takes place between ethyl cyanoacetate and *cyclo*hexanone or analogous compounds, hydrogen migrates in the ketonic substance, which behaves virtually as an enol; thus *cyclo*hexanone yields ethyl α-cyano-Δ^1-*cyclo*hexeneacetate,



$CH_2{<}{}^{CH_2-CH}_{CH_2\cdot CH_2}{>}C\cdot CH(CN)\cdot CO_2Et$, whilst benzoin gives rise to αδ-dicyano-βγ-diphenyl-Δ^β-butene-αδ-dicarboxylic acid,

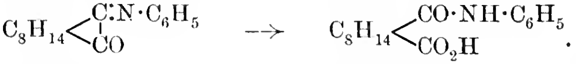
$$CO_2H\cdot CH(CN)\cdot CPh{:}CPh\cdot CH(CN)\cdot CO_2H.$$

It seems clear, however, that camphorquinone behaves differently, because when camphorylidenecyanoacetic acid is oxidised with potassium permanganate, camphoric acid is the sole product, whereas the alternative representation demanded by analogy to Haworth's experiments would certainly not lead to that substance, as the ring would probably open at the point of unsaturation, giving rise to trimethyl*cyclo*pentanonecarboxylic acid. Moreover, the derivatives of camphorquinone, if comparable with the condensation products obtained by Haworth, should contain hydrogen replacable by alkyl groups, and although the peculiar behaviour of ethyl camphorylidenecyanoacetate towards alkali renders this compound unsuitable for the test, we have ascertained that the corresponding phenylcyanomethylenecamphor cannot be alkylated.

In this connexion it may perhaps be pointed out that while there is not the slightest reason to doubt the propriety of Haworth's explanation, hydrogen available for enolisation is by no means essential to the course of such a condensation. Enolisation can scarcely be supposed to occur, for example, in benzaldehyde, although that substance undergoes condensation with ethyl cyanoacetate, and it is equally impossible in benzil, which some experiments conducted by Mr. R. T. F. Barnett have shown to yield a compound, $C_{19}H_{15}O_3N$, that is, a product of condensation between molecular proportions of the diketone and the ester.

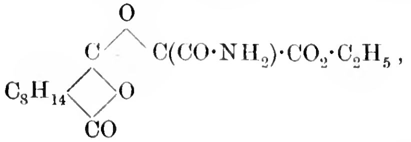
Nevertheless, it has to be admitted that the ethenoid linking in these new derivatives of camphorquinone presents curious features; for instance, addition of bromine or hydrogen bromide does not take place, and although the presence of the nucleus, $\cdot CO\cdot CX\colon CX_2$, suggests analogy to pulegone, which yields acetone and methyl*cyclo*hexanone when heated with formic acid, protracted action of the last-named substance on ethyl camphorylidenecyanoacetate does not produce a trace of camphor. Furthermore, camphorquinone has not been recovered by the action of either potassium ferricyanide or mercuric acetate, although the latter agent gives rise to the diketone when acting on enolic benzoylcamphor (Trans., 1903, **83**, 103). Moreover, it has not been possible to draw any conclusion from the behaviour of the condensation products towards hydrogen peroxide.

When the difficulty of hydrolysing the cyano-group in ethyl camphorylidenecyanoacetate was first encountered, the action of hydrogen peroxide was studied, this agent having been found applicable in some cases of transforming nitriles into amides. It has this effect on the substance under discussion, there being added, simultaneously with water, one molecular proportion of oxygen. The action is pursued in alkaline solution, and the resulting amide-ester, $C_{15}H_{21}O_6N$, is accompanied by the monobasic amide-acid, $C_{13}H_{17}O_6N$, both these substances being hydrolysed to the dibasic acid, $C_{13}H_{16}O_7$. The problem of their constitution, however, has remained unsolved, as they are extremely resistant towards chemical agents. The most likely course for the action to follow suggests the addition of oxygen to the double linking and simultaneous conversion of the camphor nucleus into a derivative of camphoric anhydride, because hydrogen peroxide rapidly transforms camphorquinone into that substance, and also, as we have recently found, converts phenyliminocamphor into camphoranilic acid:



$$C_8H_{14}<\begin{matrix}C\colon N\cdot C_6H_5\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CO\cdot NH\cdot C_6H_5\\ CO_2H\end{matrix}.$$

The amide-ester from ethyl camphorylidenecyanoacetate would accordingly be represented as having the constitution:

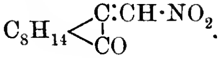


but the recent work of Prileschaeff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 609) suggests that such an oxide should be readily hydrated, yielding the glycol or its products of further hydrolysis; alkalis, however, do not bring about the alteration expected, and we are obliged to leave this part of the work in abeyance.

In conclusion, it may be stated that condensation has not been effected between camphorquinone and acetonitrile, acetophenone, ethyl phenylacetate, 1:2:4-dinitrotoluene, ethyl acetoacetate, or the monoxime of diacetyl.

EXPERIMENTAL.

Nitromethylenecamphor,



$$C_8H_{14}<\begin{matrix}C:CH\cdot NO_2\\ | \\ CO\end{matrix}.$$

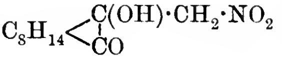
A suspension of sodionitromethane was prepared by mixing 8 grams of nitromethane with 100 c.c. of alcohol in which 3·6 grams of sodium had been dissolved; 16 grams of camphorquinone in 50 c.c. of hot alcohol were then added, when the major part of the sodium derivative disappeared. The liquid was set aside, and quickly changed to a pasty mass of bulky, indefinitely crystalline material, which, after twelve hours, was filtered, drained on earthenware, dissolved in water, and immediately acidified with dilute sulphuric acid. An oil separated, rapidly becoming crystalline, the product weighing 15 grams. Repeated extraction with 200 c.c. of hot petroleum (b. p. 60—80°) gave spherical nodules of minute, silky needles, the snow-white product obtained on recrystallisation melting at 77°:

0·1573 gave 0·3628 CO_2 and 0·1024 H_2O. C=62·90; H=7·28.
0·2627 „ 15·4 c.c. N_2 at 25° and 763·6 mm. N=6·61.
$C_{11}H_{15}O_3N$ requires C=63·12; H=7·23; N=6·70 per cent.

The substance is freely soluble in cold benzene, chloroform, or methyl alcohol, and also in sodium carbonate, from which camphorquinone is rapidly precipitated; the alcoholic solution is indifferent towards ferric chloride, which develops an intense red coloration with an aqueous solution of the sodium derivative. The latter yields with copper acetate a bulky, grass-green precipitate, insoluble in alcohol or acetone, and becoming black when suspended in boiling water. The sodium derivative, even when freshly prepared from nitromethylenecamphor and sodium ethoxide, is highly unstable towards excess of alkali, quickly becoming yellow and depositing crystals of camphorquinone within a few minutes; it is not surprising, therefore, that an aqueous solution decolorises potassium permanganate instantly, yielding camphorquinone. A solution containing 0·2446 gram of nitromethylenecamphor in chloroform, diluted to 25 c.c., gave α_D 2°35′ in a 3-dcm. tube, whence $[\alpha]_D$ 88·0°, remaining constant during twelve days; 0·2490 gram in 25 c.c. of alcohol, containing 0·12 gram of sodium per 100 c.c., gave α_D 4°0′ in a 3-dcm. tube, whence $[\alpha]_D$ 133·8°, falling to 117·1° within twenty-seven hours, and becoming inactive after the lapse of three weeks. A solution containing 0·2468 gram in 10 per cent. aqueous sodium hydroxide was colourless when freshly prepared, and gave α_D 3°5′ in a 3-dcm. tube, whence $[\alpha]_D$ 104·1°; the liquid gradually became yellow, gave $[\alpha]_D$ 47·3° after six weeks and 36·6° after seven months.

Nitromethylenecamphor does not decolorise bromine in chloroform, being deposited unchanged on evaporation; if, however, the sodium derivative is suspended in dry chloroform, the colour of the halogen is immediately discharged, and bromopicrin is formed along with a crystalline substance melting at 124°, dissolving in alkali, and yielding camphorquinone when the liquid is heated. After remaining in contact with fuming hydrobromic acid during six weeks, nitromethylenecamphor was found to be unaltered; no change occurs, moreover, when the substance is heated with aniline on the water-bath, or dissolved in 30 per cent. acetic acid containing the base, in spite of the fact that under similar conditions hydroxymethylenecamphor yields a condensation product (Bishop, Claisen, and Sinclair, *Annalen*, 1894, **281**, 331; compare also Pope and Read, Trans., 1909, **95**, 171).

αα-Nitromethylhydroxycamphor,



$C_8H_{14}<{C(OH)\cdot CH_2\cdot NO_2 \atop {\vert \atop CO}}$.

On one occasion it was noticed that the nitromethylenecamphor was accompanied by a substance considerably less readily soluble in petroleum, and it was subsequently found that a slight modification in the conditions led to a preponderating quantity of this material.

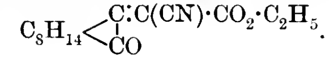
Four grams of camphorquinone and 2 grams of nitromethane were added to 25 c.c. of absolute alcohol, in which 0·1 gram of sodium had been dissolved. As there did not appear to be any change during twelve hours, a further quantity of sodium ethoxide prepared from 25 c.c. of alcohol and 0·8 gram of sodium was added, when the liquid set to a paste of crystals within one hour. After filtration the product was dissolved in water and immediately acidified with dilute sulphuric acid, which precipitated a solid instead of an oil; the melting point was constant at 104° when the substance had been recrystallised three times from boiling petroleum:

0·1534 gave 0·3284 CO_2 and 0·1008 H_2O. C=58·39; H=7·35.
0·2847 ,, 16·0 c.c. N_2 at 21° and 745 mm. N=6·29.
$C_{11}H_{17}O_4N$ requires C=58·11; H=7·55; N=6·17 per cent.

The hydroxy-compound requires about twice as much hot petroleum as nitromethylenecamphor to dissolve it (60 c.c. to 1 gram), and separates therefrom in long, silky needles. A solution containing 0·2600 gram in chloroform, made up to 25 c.c., gave

α_D 3°19′ in a 2-dcm. tube, whence $[\alpha]_D$ 159·5°. It dissolves slowly in sodium carbonate, which becomes bright yellow when warmed, from separation of camphorquinone. The nitro-compound is freely soluble in all organic media excepting petroleum.

Ethyl Camphorylidenecyanoacetate (Ethyl Methylenecamphorcyanocarboxylate),



$$C_8H_{14}\!<\!\begin{matrix}C{:}C(CN)\cdot CO_2\cdot C_2H_5\\ |\\ CO\end{matrix}.$$

Fifty grams of ethyl cyanoacetate, followed by 70 grams of camphorquinone (1 mol.), were added to 300 c.c. of absolute alcohol in which 0·5 gram of sodium had been dissolved; although not completely soluble at first, the quinone gradually passed into solution, accompanied by a noticeable rise of temperature and a slight darkening in colour. This faded, however, and separation of sulphur-yellow crystals began within one hour. Including a further deposit from the diluted mother liquor, the yield amounted to 93 grams, and as 5 grams of unused camphorquinone was recovered by still further dilution, represented 90 per cent. of the theoretical quantity. Recrystallisation from hot alcohol gave flat, lustrous, sulphur-yellow prisms, melting at 97°:

0·1536 gave 0·3878 CO_2 and 0·1022 H_2O. C = 68·86; H = 7·48.
0·3188 „ 15·0 c.c. N_2 at 22° and 776 mm. N = 5·47.
$C_{15}H_{19}O_3N$ requires C = 68·92; H = 7·33; N = 5·36 per cent.

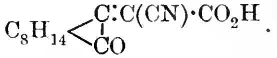
The substance is freely soluble in cold organic media excepting petroleum, which dissolves it readily when warm, depositing long, yellow, striated needles, growing together into six-sided plates. A solution containing 0·2527 gram, made up to 25 c.c. with chloroform, gave α_D 6°6′ in a 3-dcm. tube, whence $[\alpha]_D$ 201·2°; concentrated nitric acid dissolves the compound freely, the pale yellow solution remaining unaltered during many days, when water precipitates the original material. Moreover, a solution in anhydrous formic acid was boiled continuously during seven days without producing any effect beyond hydrolysis of about 5 per cent.

Action of Sulphuric Acid.—Ten grams of the finely powdered substance were dissolved in 50 grams of concentrated sulphuric acid, and after an interval of six hours poured on 125 grams of ice. The filtered liquid having been heated one hour on the steam-bath, a considerable proportion of dark brown tar separated, from which the clear liquid was decanted as soon as cold; from this there separated 4·5 grams of indefinite crystals, deposited by boiling water in snow-white needles melting at 179°, and evolving gas at about 210°:

0·1544 gave 0·3766 CO_2 and 0·0852 H_2O. C = 66·52; H = 6·18.
$C_{13}H_{14}O_4$ requires C = 66·63; H = 6·03 per cent.

We are not able to indicate the structure of this product. The empirical formula is that of camphorylidenemalonic anhydride, but it is an acid, and if it were a bimolecular acid anhydride, the molecular weight would be 486, corresponding with the formula $C_{26}H_{30}O_9$; the substance is not readily soluble in benzene, and a small proportion separated before the freezing point of the solvent was reached, but an estimation of molecular weight under these conditions gave 280. As this value is not greatly in excess of 234, required by the formula $C_{13}H_{14}O_4$, and as premature crystallisation tends to decrease the depression and thus raise the observed molecular weight, it follows that the substance is almost certainly unimolecular.

Camphorylidenecyanoacetic Acid,



$C_8H_{14}<\begin{matrix}C{:}C(CN){\cdot}CO_2H \\ | \\ CO\end{matrix}$.

Twenty grams of ethyl camphorylidenecyanoacetate were added to 150 c.c. of absolute alcohol in which 2 grams of sodium had been dissolved, when a pale brown coloration began to develop, intensifying as the crystals slowly dissolved. After fourteen days the deep brown liquid, which had not liberated ammonia, was evaporated to dryness and the residue dissolved in water, which formed a clear solution with a small proportion, becoming turbid on dilution; the liquid was therefore boiled with charcoal, filtered, cooled, acidified with dilute sulphuric acid, and extracted with ether. The latter deposited crystals on evaporation, and after the residue had remained six days in the desiccator, it was treated with a small quantity of benzene, in which it formed a clear solution, changing almost immediately into a crystalline paste; the product was therefore drained and recrystallised twice from hot benzene, which deposited lustrous, sulphur-yellow needles, melting at 141—143°:

0·1642 gave 0·4040 CO_2 and 0·0983 H_2O. C = 67·10; H = 6·70.
0·2597 „ 13·6 c.c. N_2 at 22° and 767 mm. N = 6·01.
$C_{13}H_{15}O_3N$ requires C = 66·91; H = 6·49; N = 6·01 per cent.

A solution containing 0·2630 gram in chloroform, made up to 25 c.c., gave α_D 4°42′ in a 3-dcm. tube, whence $[\alpha]_D$ 223·4°. The acid is moderately soluble in hot water, from which it separates as an oil on cooling; organic media dissolve it freely excepting petroleum, in which it is insoluble, even on boiling.

The *ammonium* salt is very readily soluble in water, crystallising in minute, pale yellow needles, and decomposing at 195°. The *silver* salt is sparingly soluble, crystallising in long, slender needles, which are moderately stable towards light. The *lead* salt is much less readily soluble, separating as a pasty mass of minute, very pale yellow needles. An aqueous solution of the ammonium salt gave a white precipitate with soluble salts of *mercury, zinc*, and *tin*, whilst *ferric* chloride developed a buff precipitate; the salts of copper, cobalt, and barium are not precipitated.

The *methyl* ester, prepared from the aqueous sodium salt and methyl sulphate, crystallised from hot petroleum in lustrous, golden-yellow needles, melting at 81°:

0·2337 gave 11·6 c.c. N_2 at 21° and 765·4 mm. N = 5·71.

$C_{14}H_{17}O_3N$ requires N = 5·67 per cent.

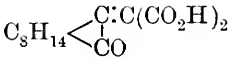
The *amide*, prepared from the ethyl ester in alcohol by the action of ammonia, crystallises from hot water in slightly yellow leaflets melting at 104°:

0·0974 gave 10·4 c.c. N_2 at 21° and 755·4 mm. N = 12·12.

$C_{13}H_{16}O_2N_2$ requires N = 12·07 per cent.

Oxidation with Potassium Permanganate.—One gram of camphorylidenecyanoacetic acid dissolved in 10 c.c. of sodium carbonate was treated with ice-cold potassium permanganate until the supernatant liquid was pink, when the equivalent of slightly more than four atoms of oxygen had been used. Proceeding subsequently as usual in such cases, a specimen of camphoric acid melting at 185° was obtained.

Camphorylidenemalonic Acid,



$C_8H_{14}<\begin{matrix}C{:}C(CO_2H)_2\\ |\\ CO\end{matrix}$

In order to convert cyanomethylenecamphor into camphorylideneacetic acid, Bishop, Claisen, and Sinclair (*loc. cit.*, 389) found it necessary to heat the nitrile in a sealed tube with glacial acetic and hydrochloric acids. Camphorylidenecyanoacetic acid is even more stable, and was recovered unchanged after being subjected to this treatment; by the use of hydrobromic acid, however, hydrolysis has been effected.

Two grams of the acid were dissolved in 12 grams of glacial acetic acid, and heated with 8 grams of hydrobromic acid (D 1·49) in a sealed tube during four hours at 140—180°. No pressure was noticeable on opening the tube, but the contents had become slightly brown, and crystals of ammonium bromide had been deposited. The liquid was poured into water and extracted with ether, from which the solid residue (0·5 gram), after recrystallisation from hot water, separated in straw-coloured needles, melting with vigorous intumescence at 206°:

0·1123 gave 0·2550 CO_2 and 0·0637 H_2O. C = 61·93; H = 6·25.

$C_{13}H_{16}O_5$ requires C = 61·87; H = 6·40 per cent.

Contrary to expectation, we could not convert this compound into Claisen's camphorylideneacetic acid.

Action of Hydrogen Peroxide on Ethyl Camphorylidenecyanoacetate.

Twenty-five grams of the ester were dissolved in 150 c.c. of hot alcohol, which was then cooled rapidly and treated with 225 c.c. of hydrogen peroxide ("20 vols.") in quantities of 40—50 c.c., the alkalinity of the liquid being maintained by adding a few drops of sodium hydroxide from time to time. The crystals quickly dissolved, and when the colour had faded with the last portion of hydrogen peroxide, colourless crystals began to separate; 200 c.c. of water were then added, and the cooled liquid filtered after two hours. Fifteen grams of snow-white material were obtained, crystallising from hot alcohol in lustrous prisms melting and evolving gas at 209°:

0·1400 gave 0·2964 CO_2 and 0·0876 H_2O. C = 57·74; H = 7·00.
0·3155 „ 12·3 c.c. N_2 at 22° and 776 mm. N = 4·53.
$C_{15}H_{21}O_6N$ requires C = 57·88; H = 6·75; N = 4·50 per cent.

The substance is soluble in boiling water, and requires about 10 c.c. of boiling alcohol per gram to dissolve it. A 1 per cent. solution in chloroform appeared inactive when viewed through a 3-dcm. tube.

In association with this amide-ester there is produced an equal proportion of the corresponding amide-acid. On evaporating to small bulk the filtrate from the first-named substance, allowing it to remain twenty-four hours, adding a small quantity of water, and filtering from 1 gram of the amide-ester, dilute sulphuric acid gave a white, crystalline precipitate weighing 12 grams; the substance melted and evolved gas at 138°, then solidified, and fused finally at about 203°. Recrystallisation from hot water or from absolute alcohol gave lustrous, transparent, six-sided plates, melting at 205°, when the acid turns brown and liberates gas:

0·1300 gave 0·2497 CO_2 and 0·0775 H_2O. C = 52·39; H = 6·67.
0·2301 „ 9·4 c.c. N_2 at 21·5° and 747·4 mm. N = 4·58.
$C_{13}H_{19}O_7N$ requires C = 51·83; H = 6·31; N = 4·65 per cent.

Titration with $N/10$-sodium hydroxide showed the substance to be monobasic, assuming the molecular weight 301; hence it appears to have the composition $C_{13}H_{17}O_6N + H_2O$, a small proportion of the crystallisation water having been removed in the desiccator, since the formula $C_{13}H_{17}O_6N$ requires C = 55·1, H = 6·0, and N = 4·9 per cent.

The same substance has been obtained by the action of hydrogen peroxide on camphorylidenecyanoacetic acid, and also by the incomplete hydrolysis of the amide-ester, complete hydrolysis leading to the dibasic acid. A solution of the amide-acid in alcohol, made up to 25 c.c. containing 0·2536 gram, gave α_D 0°22′ in a 3-dcm. tube, whence $[\alpha]_D$ 12·6°.

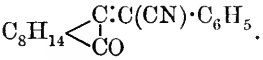
The Dibasic Acid, $C_{13}H_{16}O_7$.—Fourteen grams of the amide-ester were covered with 20 grams of 20 per cent. aqueous sodium hydroxide, when a clear solution was formed, and ammonia liberated from the hot liquid. After sixteen hours on the water-bath ammonia was no longer noticeable, and the acidified solution having been extracted eight times with ether, about 10 grams of crystalline residue were obtained on evaporating the latter. On being twice recrystallised from the minimum quantity of boiling water, colourless, transparent prisms were deposited, melting with vigorous intumescence at 231^{c}, when the substance became dark brown:

0·1286 gave 0·2572 CO_2 and 0·0679 H_2O. C=54·55; H=5·91.

$C_{13}H_{16}O_7$ requires C=54·90; H=5·68 per cent.

On titration with *N*/10-sodium hydroxide, the acid was found to be dibasic, assuming the molecular weight 284. A solution containing 0·2536 gram in alcohol, made up to 25 c.c., gave α_D −0°45′ in a 3-dcm. tube, whence $[\alpha]_D$ −24·6°. Continued heating with concentrated aqueous alkali or boiling pyridine left the substance unchanged, whilst hot alcoholic alkali gave rise to an indefinite, resinous material.

Phenylcyanomethylenecamphor,



$$C_8H_{14}<\begin{matrix}C{:}C(CN)\cdot C_6H_5\\ |\\ CO\end{matrix}.$$

Fifteen grams of phenylacetonitrile were added to 100 c.c. of absolute alcohol in which 3 grams of sodium had been dissolved; 20 grams of camphorquinone were stirred into the liquid, rapidly forming a clear solution, from which crystals began to separate within half-an-hour. The first crop weighed more than 20 grams, requiring about 400 c.c. of boiling alcohol for recrystallisation, when sulphur-yellow prisms were obtained melting at 167°:

0·1448 gave 0·4335 CO_2 and 0·0966 H_2O. C=81·65; H=7·47.

0·2781 „ 12·8 c.c. N_2 at 19° and 754 mm. N=5·26.

$C_{18}H_{19}ON$ requires C=81·46; H=7·22; N=5·28 per cent.

A solution containing 0·2608 gram in chloroform, made up to 25 c.c., gave α_D 7°42′ in a 3-dcm. tube, whence $[\alpha]_D$ 246°. Continued heating with methyl iodide in presence of sodium methoxide (1 mol.) left the substance unaltered; hence there is not a replaceable atom of hydrogen associated with the carbon which carries the cyano-group.

Action of Alcoholic Alkali.—Five grams of phenylcyanomethylenecamphor were heated with 50 c.c. of alcohol and 10 c.c. of 20 per cent. sodium hydroxide solution under reflux, when the suspended crystals gradually disappeared and the yellow colour faded. On pouring the mixture into water after two hours, 5·6 grams of a white solid separated, and was recrystallised from diluted alcohol, which deposited transparent plates melting at 97°; the fused material became solid again forthwith, melting finally at 156°, and an unheated specimen which had been left in a desiccator melted first at 158°:

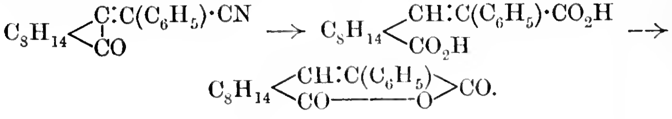
0·1553 gave 0·4354 CO_2 and 0·1079 H_2O. C = 76·47; H = 7·77.
0·2316 „ 10·1 c.c. N_2 at 22° and 756·7 mm. N = 4·93.
$C_{18}H_{21}O_2N$ requires C = 76·27; H = 7·48; N = 4·95 per cent.

The amide dissolves in concentrated sulphuric acid, but is precipitated therefrom unchanged; it is also indifferent towards hydrogen peroxide in the cold or on warming. The substance is freely soluble in chloroform, alcohol, or benzene, but dissolves only sparingly in hot petroleum, crystallising in minute, silky needles on cooling; a solution containing 0·2609 gram in chloroform, made up to 25 c.c., gave α_D 5°52′ in a 2-dcm. tube, whence $[\alpha]_D$ 281·1°.

Action of Concentrated Sulphuric Acid.—Five grams of finely powdered phenylcyanomethylenecamphor were added to 25 grams of concentrated sulphuric acid, and after an interval of six hours poured on ice. The filtered liquid was heated on the water-bath until turbid, allowed to cool, and decanted from a honey-like mass; this was kneaded with a small quantity of cold water, which changed it into a milky fluid, slowly depositing a colourless solid. After extraction with sodium carbonate, which removed but little acid material, the residue was dissolved in a small quantity of hot alcohol, precipitated with water, and recrystallised from boiling alcohol, which deposited lustrous, transparent prisms, melting at 204°:

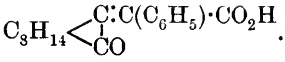
0·1593 gave 0·4437 CO_2 and 0·1029 H_2O. C = 75·96; H = 7·23.
$C_{18}H_{20}O_3$ requires C = 76·01; H = 7·10 per cent.

Thus the substance is isomeric with camphorylidenephenylacetic acid, and it probably arises from the opening of the camphor ring, followed by anhydride formation between the resulting carboxyl group and that produced from hydrolysing the nitrile:



$$C_8H_{14}\Big<\begin{matrix}C{:}C(C_6H_5)\cdot CN\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}\Big<\begin{matrix}CH{:}C(C_6H_5)\cdot CO_2H\\ CO_2H\end{matrix} \longrightarrow C_8H_{14}\Big<\begin{matrix}CH{:}C(C_6H_5)\\ CO\text{———}O\end{matrix}\Big>CO.$$

Camphorylidenephenylacetic Acid,



$C_8H_{14}<\begin{matrix}C{:}C(C_6H_5){\cdot}CO_2H \\ | \\ CO\end{matrix}$.

The foregoing amide was found to resist the further action of alkali, for after heating with alcoholic sodium hydroxide during three days the major portion was recovered on diluting with water; on acidifying the mother liquor, however, a small amount of flocculent, yellow matter separated, and proved to be the expected carboxylic acid.

This is more readily obtained by the action of nitrous acid on the amide. A solution of 1 gram in 10 c.c. of concentrated sulphuric acid was diluted with 10 c.c. of water, cooled in ice, and treated with 0·5 gram of sodium nitrite in a small quantity of water; a solid was at once precipitated, and to complete the action the mixture was heated on the steam-bath, then diluted with water, and filtered. The product crystallised from diluted alcohol in faintly straw-coloured needles melting at 186°; it is scarcely charred at 250°, and in this respect recalls camphorylideneacetic acid, which may even be distilled without undergoing change (Bishop, Claisen, and Sinclair, *loc. cit.*):

0·1562 gave 0·4354 CO_2 and 0·0983 H_2O. $C=76·02$; $H=7·04$.

$C_{18}H_{20}O_3$ requires $C=76·01$; $H=7·10$ per cent.

The acid dissolves freely in cold benzene, ethyl acetate, methyl alcohol, or glacial acetic acid, but is insoluble in boiling petroleum; a solution containing 0·2518 gram in chloroform, made up to 25 c.c., gave α_D 4°42′ in a 2-dcm. tube, whence $[\alpha]_D$ 233·3°.

Action of Hydrogen Peroxide on Phenylcyanomethylenecamphor.

Phenylcyanomethylenecamphor (2·65 grams) dissolved in hot alcohol (30 c.c.) was treated with hydrogen peroxide (30 c.c. of "20 vols.") and 20 per cent. sodium hydroxide (4 c.c.) added in four or five portions during the course of fifteen minutes. The colour faded somewhat, and the liquid, which remained clear, was poured on ice and acidified with dilute hydrochloric acid; the white precipitate was recrystallised from diluted alcohol, forming well-defined, rhombic prisms melting at 153°:

0·1588 gave 0·4051 CO_2 and 0·1133 H_2O. $C=69·59$; $H=7·80$.

0·2613 „ 9·6 c.c. N_2 at 21° and 746·5 mm. $N=4·12$.

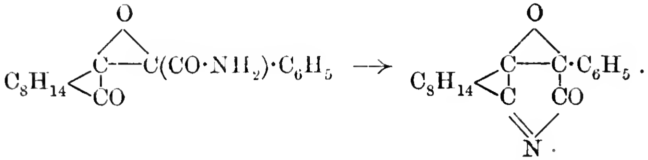
$C_{18}H_{21}O_3N+C_2H_6O$ requires $C=69·52$; $H=7·88$; $H=4·06$ per cent.

Whilst cold acetone, chloroform, or ethyl acetate dissolve the substance freely, it is less readily soluble in benzene or methyl alcohol, crystallising from the former in lustrous, transparent, rectangular prisms; it is insoluble in boiling petroleum.

Action of Concentrated Sulphuric Acid.—The solution in concentrated sulphuric acid was ruby-coloured, and yielded a bright yellow solid when poured on ice; repeated crystallisation from diluted alcohol gave bright yellow prisms melting at 161°:

0·0986 gave 0·2776 CO_2 and 0·0624 H_2O. C=76·78; H=7·08.
0·1386 ,, 6·3 c.c. N_2 at 22° and 752 mm. N=5·11.
$C_{18}H_{19}O_2N$ requires C=76·82; H=6·81; N=4·98 per cent.

Hence it appears that the substance has been converted into an internal anhydride, which might possibly arise in the following manner:



It is freely soluble in organic media excepting petroleum, which dissolves it when heated, and deposits slender, silky needles on cooling. Boiling water does not dissolve it, but it is readily soluble in warm alkali, forming a yellow solution, which rapidly becomes colourless and yields a yellow precipitate when acidified.

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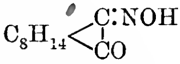
CXLII.—*Studies in the Camphane Series. Part XXXII. Stereoisomeric Modifications of* iso*Nitrosoepicamphor, the Third and Fourth Monoximes of Camphorquinone.*

By Martin Onslow Forster and Hans Spinner.

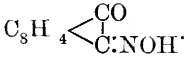
According to the usually accepted representation of camphorquinone, based on Bredt's formula for camphor, accumulated information concerning the oxime class involves the prediction of four dioximes and four monoximes, the asymmetry of the trimethyl*cyclo*pentane nucleus with regard to the biscarbonyl group in camphorquinone opening the way to one dioxime and two monoximes in excess of those which correspond with the dioximes and monoximes of benzil. This expectation may be held as independent of the Hantzsch-Werner hypothesis, and would operate to the same extent on the supposition that oxime isomerism is structural instead of geometrical.

At the present time there have been isolated six among the eight hypothetical oximino-derivatives of camphorquinone. Three dioximes were prepared by Manasse from *iso*nitrosocamphor and hydroxylamine (*Ber.*, 1893, **26**, 243), and the fourth was isolated subsequently from the same source (Forster, Trans., 1903, **83**, 514). The best-known monoxime of camphorquinone is *iso*nitrosocamphor, discovered by Claisen and Manasse (*Ber.*, 1889, **22**, 530, and *Annalen*, 1893, **274**, 71), who subjected camphor dissolved in ether to the successive action of sodium and *iso*amyl nitrite. The original product of this action was shown to be a mixture containing, in addition to the stable oxime (m. p. 152°), an unstable isomeride, the second monoxime of camphorquinone, melting at 114° (Forster, *loc. cit.*, 534, and Trans., 1904, **85**, 904); thus there remain unknown two monoximes, having the relationship to epicamphor (Lankshear and W. H. Perkin, Proc., 1911, **27**, 166; Bredt and Hilbing, *Chem. Zeit.*, 1911, **35**, 765) borne by the known ones to camphor itself:



$C_8H_{14}<\begin{array}{l}C{:}NOH\\ |\\ CO\end{array}$

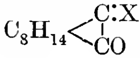
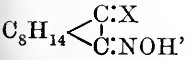
*iso*Nitrosocamphor
(two forms known).



$C_8H_{14}<\begin{array}{l}CO\\ |\\ C{:}NOH\end{array}$

*iso*Nitrosoepicamphor
(two forms wanting).

During the past eight years numerous attempts have been made in this laboratory to isolate these missing oximes, which might become the source of epicamphor. Although the recent discovery of the latter substance has deprived the work of this incentive, the difficulty of preparing the new ketone in any considerable quantity rendered a continuance of the experiments desirable, and we are now able to describe a process for obtaining the third and fourth monoximes of camphorquinone independently of epicamphor.

The general principle underlying the experiments which have hitherto failed was based on the expectation that a camphor derivative of the type  $C_8H_{14}<\begin{array}{l}C{:}X\\ |\\ CO\end{array}$, after conversion into the oxime  $C_8H_{14}<\begin{array}{l}C{:}X\\ |\\ C{:}NOH\end{array}$, might be led to exchange X for oxygen; but it has always happened that when the initial compound is of a character which permits a smooth elimination of the group X, its behaviour towards hydroxylamine results in an exchange of X for the oximino-group, with consequent production of *iso*nitrosocamphor or the β-dioxime of camphorquinone. This has been shown in connexion with the *N*-methyl ether of *iso*nitrosocamphor (Trans., 1904, **85**, 898), iminocamphor (Trans., 1905, **87**, 832), and its aryl derivatives (Trans., 1909, **95**, 942), evidence having been adduced

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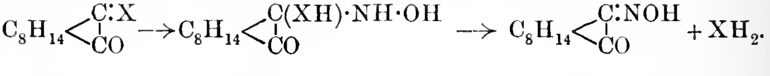
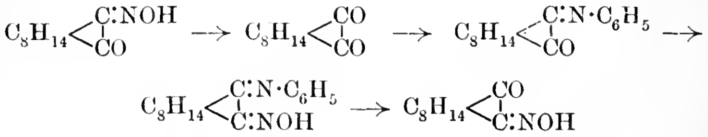
to indicate that the formation of *iso*nitrosocamphor from these compounds is preceded by addition of hydroxylamine:



$$C_8H_{14}<\begin{matrix}C{:}X\\ |\\ CO\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}C(XH){\cdot}NH{\cdot}OH\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C{:}NOH\\ |\\ CO\end{matrix} + XH_2.$$

Camphorquinonephenylhydrazone, on the other hand, although yielding an oxime (Trans., 1909, **95**, 955), contains the phenylhydrazine residue attached to carbon so firmly that attempts to eliminate it without disturbing the oximino-group were unsuccessful. Another failure has been recorded in connexion with α-triazocamphoroxime (Trans., 1907, **91**, 874), and many unpublished experiments in the same direction have also been fruitless.

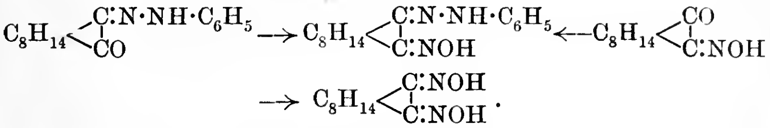
We now find that although phenyliminocamphor yields *iso*nitrosocamphor with hydroxylamine hydrochloride and sodium acetate, action proceeds in the required direction when sodium hydroxide is substituted for the salt, the product consisting of two stereoisomeric oximes, $C_8H_{14}<\begin{smallmatrix}C{:}N{\cdot}C_6H_5\\ |\\ C{:}NOH\end{smallmatrix}$; these may be separated by fractional crystallisation, the α-oxime being colourless or sometimes very pale brown, melting at 174° and having $[\alpha]_D$ 304·4° in chloroform, whilst the β-oxime is yellow, melts at 112°, and has $[\alpha]_D$ 335·4°. The β-oxime dissolves freely in cold dilute hydrochloric acid forming an almost colourless solution, from which, after a few minutes, there begin to separate lustrous, fern-like crystals of *iso*nitrosoepicamphor, which is thus producible from *iso*nitrosocamphor by the following steps:



$$C_8H_{14}<\begin{matrix}C{:}NOH\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CO\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C{:}N{\cdot}C_6H_5\\ |\\ CO\end{matrix} \longrightarrow$$

$$C_8H_{14}<\begin{matrix}C{:}N{\cdot}C_6H_5\\ |\\ C{:}NOH\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CO\\ |\\ C{:}NOH\end{matrix}$$

The product, β-*iso*nitrosoepicamphor, melts at 137°, then becomes semi-solid, and is not clear below 160°; it is therefore an unstable modification, and may be transformed into the stable isomeride, α-*iso*nitrosoepicamphor, by boiling water, from which it separates in long, lustrous needles, melting at 170°. A mixture of these two forms does not begin to melt below 137°, and is not completely fused below 160°, so that their behaviour is exactly comparable with that of the unstable and stable varieties of *iso*nitrosocamphor. The solution of each isomeride in alkali hydroxide is intensely yellow, and when diluted gives with ferrous sulphate a deep bluish-violet precipitate resembling that developed by the two forms of *iso*nitrosocamphor. With phenylhydrazine hydrochloride both modifications of *iso*nitrosoepicamphor yield an oxime of camphorquinonephenylhydrazone, whilst hydroxylamine acetate converts them into dioximes of camphorquinone:

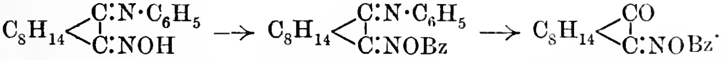


$$C_8H_{14}<\begin{array}{l}C{:}N\cdot NH\cdot C_6H_5\\ CO\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}N\cdot NH\cdot C_6H_5\\ C{:}NOH\end{array} \leftarrow C_8H_{14}<\begin{array}{l}CO\\ C{:}NOH\end{array}$$

$$\rightarrow C_8H_{14}<\begin{array}{l}C{:}NOH\\ C{:}NOH\end{array}.$$

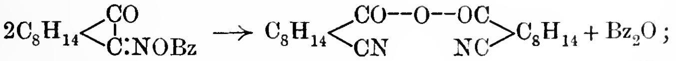
These changes, taken in conjunction with the origin of the materials, serve to establish the position of the oximino-group. Moreover, it was announced by Bredt and Perkin (Proc., 1912, **28**, 56), simultaneously with the preliminary notice of these experiments, that they have prepared the same two *iso*nitroso-derivatives from epicamphor itself, so that no doubt remains as to the relationship of the third and fourth monoximes of camphorquinone to that substance.*

On comparing the new oximes with the two already known, the points of resemblance are found to be more numerous than the distinctions. Among the latter, however, must be noted the superior activity of the free carbonyl group, which undergoes oximation and conversion into a phenylhydrazone with the greatest ease. Furthermore, whereas only the unstable *iso*nitrosocamphor yields a yellow benzoyl derivative from which it may be regenerated by hydrolysis, whilst the benzoyl compound from the stable form is colourless, and changes to cyanolauronic acid when hydrolysed, each *iso*nitroso-derivative of epicamphor yields a benzoyl compound, one yellow and one colourless, from which the respective oxime may be regenerated by alkali. These benzoyl derivatives can be prepared also from the corresponding oxime of phenyliminocamphor by benzoylation and removal of aniline with acid:



$$C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_5\\ C{:}NOH\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_5\\ C{:}NOBz\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CO\\ C{:}NOBz\end{array}.$$

One specimen of benzoyl-β-*iso*nitrosoepicamphor, although preserved in darkness, changed spontaneously into the anhydrides of benzoic and β-camphornitrilic acids:



$$2C_8H_{14}<\begin{array}{l}CO\\ C{:}NOBz\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CO{-}{-}O{-}{-}OC\\ CN\qquad\qquad NC\end{array}>C_8H_{14} + Bz_2O;$$

this corresponds with the decomposition of the colourless and yellow derivatives of *iso*nitrosocamphor under the influence of light, whereby the anhydrides of benzoic and cyanolauronic acids

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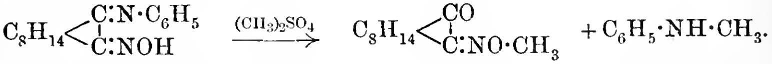
* In the abstract of this paper (Proc., 1912, **28**, 46), the more readily fusible phenyliminocamphoroxime was entitled the α-oxime, but since Bredt and Perkin (*loc. cit.*) refer to the more readily fusible *iso*nitrosoepicamphor as the β-isomeride, we have inverted our previous arrangement in order to avoid confusion.—M.O.F.

are produced (Trans., 1904, **85**, 907), but the same alteration in benzoyl-α-*iso*nitrosoepicamphor has not yet been observed.

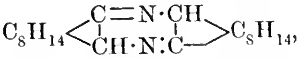
The methylation of *iso*nitrosocamphor led to a single *O*-methyl ether associated with the isomeric *N*-methyl derivative, the *O*-methyl ether yielding only cyanolauronic acid on hydrolysis. The case of *iso*nitrosoepicamphor is somewhat different. Whilst methylation of the α-modification proceeds on the above lines, giving principally the *N*-methyl derivative, together with a small proportion of the colourless *O*-methyl ether which breaks down to β-camphornitrilic acid on hydrolysis, β-*iso*nitrosoepicamphor yields principally the yellow *O*-methyl ether, from which likewise the *iso*nitroso-derivative cannot be regenerated, β-camphornitrilic acid being the sole product of hydrolysis. In this connexion it is noteworthy that, whilst the β-oxime of phenyliminocamphor remains for the most part unaffected by methyl sulphate in presence of aqueous sodium hydroxide, the α-oxime is transformed into methylaniline and the colourless *O*-methyl ether of *iso*nitrosoepicamphor:



$$C_8H_{14}\Big<\begin{array}{l}C{:}N\cdot C_6H_5\\ |\\ C{:}NOH\end{array} \xrightarrow{(CH_3)_2SO_4} C_8H_{14}\Big<\begin{array}{l}CO\\ |\\ C{:}NO\cdot CH_3\end{array} + C_6H_5\cdot NH\cdot CH_3.$$

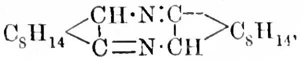
This observation may have some bearing on the configuration of the two new oximes of camphorquinone, as the immunity of phenyliminocamphor-β-oxime certainly suggests steric hindrance to the methylation of the *iso*nitroso-group.

The reduction of *iso*nitrosoepicamphor with zinc dust in alkaline solution proceeds very readily, leading to aminoepicamphor, brief notice of which is given by Bredt and Perkin (*loc. cit.*). Both modifications yield the same base, and bearing in mind the superior reactivity of the unoximated carbonyl group, it is noteworthy that the reduction process does not extend to this also, and lead to aminoepiborneol; this is the more remarkable when it is remembered that phenyliminocamphor only requires to be shaken in ethereal solution with zinc dust to undergo reduction to phenylaminocamphor. The usual typical derivatives of the base have been characterised, and also aminoepicamphoroxime, which is formed much more easily than aminocamphoroxime from α-aminocamphor. Moreover, the auto-condensation of aminoepicamphor proceeds very rapidly, and the resulting epidihydrodicamphenepyrazine,



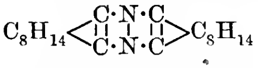
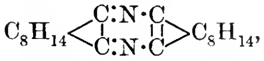
$$C_8H_{14}\Big<\begin{array}{l}C{=}N\cdot CH\\ |\qquad\quad |\\ CH\cdot N{:}C\end{array}\Big>C_8H_{14},$$

isomeric with the dihydrodicamphenepyrazine obtained by Duden and Pritzkow (*Annalen*, 1899, **307**, 208) from α-aminocamphor,



$$C_8H_{14}\Big<\begin{array}{l}CH\cdot N{:}C\\ |\qquad\quad |\\ C{=}N\cdot CH\end{array}\Big>C_8H_{14},$$

yields the same dicamphenepyrazine on oxidation. It is not possible, however, to decide between the two formulæ:

 and 

$$C_8H_{14}<\begin{array}{c}C\cdot N\cdot C\\ \| \quad | \quad \| \\ C\cdot N\cdot C\end{array}>C_8H_{14} \quad \text{and} \quad C_8H_{14}<\begin{array}{c}C{:}N\cdot C\\ | \qquad \| \\ C{:}N\cdot C\end{array}>C_8H_{14},$$

suggested respectively by Duden and Pritzkow, Einhorn and Jahn (*Ber.*, 1902, **35**, 3657) for the representation of dicamphenepyrazine. At first it seemed probable that some conclusion might be drawn from the specific rotatory power, for whilst epidihydrodicamphenepyrazine and dihydrodicamphenepyrazine have $[\alpha]_D$ 425·5° and $-283·3°$ respectively, that of dicamphenepyrazine is only 55·5°; but reflection will show that this low rotation might be due either to disappearance of the azethenoid linkings indicated in the first formula, or to compensation of one such linking in the α-position by another in the lower, a similar peculiarity having been observed in connexion with camphaneoxytriazine,  $C_8H_{14}<\begin{array}{l}C{:}N\cdot NH\\ | \qquad\quad | \\ C{:}N\cdot CO\end{array}$, which has $[\alpha]_D$ 22·6°.

EXPERIMENTAL.

The Oximes of Phenyliminocamphor,  $C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_5\\ | \\ C{:}NOH\end{array}$

Twenty-five grams of phenyliminocamphor dissolved in 400 c.c. of alcohol (96 per cent.) were treated successively with 12·5 grams of powdered sodium hydroxide (Kahlbaum) and 14·5 grams of hydroxylamine hydrochloride; after being heated under reflux during two hours, the product was filtered into 3000 c.c. of cold water and allowed to remain for twelve hours, when 22 grams of pale yellow, crystalline material were collected. Departure from these conditions led to greatly impaired yields, and in the preliminary experiments it was found that this arose from either continued heating or from increased concentration of the solution; furthermore, if the alcoholic liquid is not filtered before dilution, the small proportion of unchanged alkali appears to prevent complete precipitation of the oximes.

The product obtained in this way is a mixture of the α- and β-oximes, melting at 174° and 112° respectively (see footnote, p. 1343). It has been the practice to extract it in quantities of 40 grams with petroleum (b. p. 60—80°) in a Soxhlet apparatus, about 11 grams of the less fusible form remaining in the thimble whilst the isomeride crystallises from the solvent as it cools; recrystallisation of this modification from hot alcohol gives massive, transparent, sulphur-yellow prisms, melting at 112°:

0·1691 gave 0·4631 CO_2 and 0·1224 H_2O. $C=74·69$; $H=8·10$.
0·2152 „ 20·5 c.c. N_2 at 21° and 765·7 mm. $N=10·97$
$C_{16}H_{20}ON_2$ requires $C=74·95$; $H=7·87$; $N=10·94$ per cent.

The β-oxime is freely soluble in benzene or chloroform, dissolving readily in alcohol or petroleum when these are heated; 0·2646 gram in chloroform, made up to 25 c.c., gave α_D 7°6′ in a 2-dcm. tube, whence $[\alpha]_D$ 335·4°.

On attempting to methylate it by the action of methyl sulphate on a suspension in 10 per cent. sodium hydroxide, a very faint odour of methylaniline became noticeable after continued agitation; nevertheless, more than 90 per cent. of the original material was recovered unaltered, and it was not found possible to recognise a methyl derivative in the mother liquor.

The *benzoyl* derivative,  $C_8H_{14}<\begin{matrix}C:N\cdot C_6H_5\\ | \\ C:NOBz\end{matrix}$, prepared by the pyridine method, remained viscid after several washings, but rapidly hardened when sown; recrystallisation from petroleum, followed by diluted methyl alcohol, gave sulphur-yellow, flat, transparent prisms melting at 119°:

0·2229 gave 15·8 c.c. N_2 at 19° and 753·6 mm. N = 8·11.
$C_{23}H_{24}O_2N_2$ requires N = 7·78 per cent.

The substance dissolves freely in chloroform, methyl alcohol, or hot petroleum; a solution containing 0·2648 gram in chloroform, made up to 25 c.c., gave α_D 6°32′ in a 2-dcm. tube, whence $[\alpha]_D$ 308·4°.

On attempting to hydrolyse this compound to the benzoyl derivative of *iso*nitrosoepicamphor, cold aqueous hydrochloric acid was found to leave the major portion unaltered after many days, although aniline could be detected in the filtrate. Accordingly, the substance was suspended in alcoholic hydrochloric acid

$$(3HCl : 7C_2H_6O),$$

forming a clear solution when warmed; dilution with water precipitated pale yellow needles melting at 80° after recrystallisation from dilute alcohol, and thus identical with the benzoyl derivative of β-*iso*nitrosoepicamphor (see below). It is necessary to precipitate the benzoyl compound immediately; otherwise the hydrolysis proceeds further, yielding ethyl benzoate and *iso*nitrosoepicamphor.

The *phenylurethane* was purified with difficulty, and crystallised from alcohol in tufts of bright yellow needles melting at 143°:

0·1944 gave 19·5 c.c. N_2 at 23° and 767·2 mm. N = 11·48.
$C_{23}H_{25}O_2N_3$ requires N = 11·20 per cent.

A solution containing 0·2165 gram in chloroform, made up to 25 c.c., gave α_D 3°12′ in a 2-dcm. tube, whence $[\alpha]_D$ 184·7°.

The *α-oxime* of phenyliminocamphor, although produced in smaller proportion than the isomeride, is less difficult to isolate, as it is freed completely from the latter in the manner described.

Final recrystallisation from alcohol yields colourless or very pale brown, lustrous prisms or needles, melting at 174°:

0·2496 gave 0·6847 CO_2 and 0·1773 H_2O. C = 74·82; H = 7·95.
0·1444 „ 14·5 c.c. N_2 at 24° and 746·5 mm. N = 11·13.
$C_{16}H_{20}ON_2$ requires C = 74·95; H = 7·87; N = 10·94 per cent.

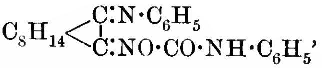
The substance is readily soluble in alcohol and in hot benzene, but boiling petroleum dissolves it only very sparingly; it is less freely soluble than the β-modification in cold benzene or chloroform. A solution containing 0·2608 gram in chloroform, made up to 25 c.c., gave α_D 6°21′ in a 2-dcm. tube, whence $[\alpha]_D$ 304·4°. An intimate mixture of the isomerides in equal quantities became pasty at 112°, but not before, and the temperature could be raised above 160° before a clear liquid was produced.

The *benzoyl* derivative, prepared as from the isomeride, solidified rapidly; it was recrystallised from benzene diluted with petroleum, and finally from benzene alone, forming very pale brown, transparent, rhomboidal prisms, melting at 141°:

0·2194 gave 15·6 c.c. N_2 at 20° and 755 mm. N = 8·11.
$C_{23}H_{24}O_2N_2$ requires N = 7·78 per cent.

The substance dissolves freely in chloroform or benzene, but is only sparingly soluble in hot petroleum; a solution containing 0·2596 gram in chloroform, made up to 25 c.c., gave α_D 6°32′ in a 2-dcm. tube, whence $[\alpha]_D$ 314·6°.

On hydrolysing the benzoyl derivative with alcoholic hydrochloric acid of the same strength as that used for the isomeride, colourless crystals began to separate before dissolution was complete, but only 2 grams were obtained from 7 grams; after recrystallisation twice from benzene diluted with the same volume of petroleum, there separated colourless, lustrous leaflets melting at 122·5°, not depressed by admixture with the benzoyl derivative of α-*iso*nitrosoepicamphor (see below).

The *phenylurethane*,  $C_8H_{14}<\begin{array}{l}C{:}N{\cdot}C_6H_5\\ \;|\\ C{:}NO{\cdot}CO{\cdot}NH{\cdot}C_6H_5\end{array}$, prepared by suspending 2·1 grams of finely powdered oxime in 30 c.c. of dried benzene and allowing it to dissolve gradually under the influence of 1 gram of phenylcarbimide, formed slightly greenish-yellow plates, melting and decomposing at 113°, after being several times recrystallised from alcohol:

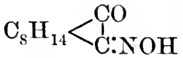
0·1727 gave 0·4503 CO_2 and 0·1200 H_2O. C = 71·11; H = 7·78.
0·1644 „ 14·4 c.c. N_2 at 21° and 767·3 mm. N = 10·12.
$C_{23}H_{25}O_2N_3,C_2H_6O$ requires C = 71·21; H = 7·42; N = 9·98 per cent.

It is freely soluble in benzene or in boiling alcohol, but only moderately so in hot petroleum. A solution containing 0·2437 gram in chloroform, made up to 25 c.c., gave α_D 4°3′ in a 2-dcm. tube, whence $[\alpha]_D$ 207·7°.

Attempt to Methylate the Oxime.—Four grams of the finely powdered α-oxime, when suspended in 50 c.c. of 10 per cent. sodium hydroxide, changed during fifteen minutes into a paste of slender, pale yellow needles consisting of the sodium derivative, and aniline was not liberated. On shaking with 10 grams of methyl sulphate the oily product rapidly became more viscous and had the odour of methyl sulphate only, but after a brief interval it became quite limpid, whilst the odour of methylaniline was increasingly noticeable. Finally, colourless, transparent prisms began to separate; after filtering the solid from the basic by-product, hot petroleum removed 2 grams of readily soluble material, leaving 1 gram of unchanged oxime. After being twice recrystallised from hot petroleum, the substance melted at 100°, not depressed by admixture with the *O*-methyl ether of α-*iso*nitrosoepicamphor (see below).

Action of Hydrochloric Acid on the Phenyliminocamphoroximes.—One gram of the β-oxime dissolved immediately in 5 c.c. of hydrochloric acid diluted with the same bulk of water, the liquid being colourless, and becoming yellow when heated to boiling; on cooling and extracting with ether the latter removed camphorquinone, whilst the colourless acid liquid, when rendered alkaline, yielded aniline and reduced Fehling's solution. Sodium carbonate extracted β-camphornitrilic acid (m. p. 109°) from the ether, whilst sodium hydroxide removed *iso*nitrosoepicamphor. The α-oxime did not dissolve in hydrochloric acid under similar conditions, becoming transformed into a colourless paste consisting of the hydrochloride, dissociated by water. When heated to 100°, however, the paste dissolved, and the liquid, treated as above, yielded the same products as the β-oxime.

The iso*Nitroso-derivatives of Epicamphor*,



$$C_8H_{14}<\begin{matrix}CO\\ |\\ C:NOH\end{matrix}.$$

Ten grams of the β-oxime of phenyliminocamphor were finely powdered and rubbed in a mortar with 100 c.c. of dilute hydrochloric acid prepared from 30 c.c. of the concentrated acid; the colourless solution was filtered immediately, for within ten minutes crystals began to separate. After two hours the product, consisting of slender, lustrous plates, was filtered and washed with water, which appeared to disintegrate and harden the material as if the initial separation had consisted of a readily dissociated hydrochloride. When freshly washed and drained on porous tile, the *iso*nitroso-compound melted at 72°, and appeared to liberate gas at about 100°; as this has been observed many times, we believe that a hydrate is formed first and loses water in the desiccator, because the temperature of fusion gradually rises until, after one week, it reaches 137°:

0·2498 gave 17·4 c.c. N_2 at 23° and 758·4 mm. N=7·89.
$C_{10}H_{15}O_2N$ requires N=7·74 per cent.

The substance was then dissolved in 10 per cent. aqueous sodium hydroxide, and precipitated therefrom with carbon dioxide; again the freshly filtered material melted at 72°, but after twenty-four hours in the desiccator melted at 137°. It was accordingly recrystallised from hot petroleum (b. p. 60—80°), in which it is freely soluble (1:8·4), separating in fern-like aggregates melting at 140°:

0·1636 gave 0·3975 CO_2 and 0·1246 H_2O. C=66·27; H=8·52.
0·1175 ,, 8·2 c.c. N_2 at 22° and 763 mm. N=7·98.
$C_{10}H_{15}O_2N$ requires C=66·25; H=8·35; N=7·74 per cent.

β-iso*Nitrosoepicamphor* is volatile in steam, and moderately soluble in hot water; it dissolves freely in cold alcohol, chloroform, and benzene. A solution containing 0·2613 gram in chloroform, made up to 25 c.c., gave $\alpha_D - 3°45'$ in a 2-dcm. tube, whence $[\alpha]_D$ −179·4°, rising to $[\alpha]_D$ −191·4° in the course of seven days, probably owing to incomplete transformation into the more stable isomeride; the higher specific rotatory power of the latter, however, was not attained, even after the lapse of four weeks.

The *benzoyl* derivative is most conveniently prepared by the Schotten-Baumann process, as a tendency to remain viscid, noticeable in this case, becomes very marked when benzoylation is effected in pyridine. Recrystallisation from diluted methyl alcohol gave lustrous, pale yellow needles melting at 80°, and becoming dark on exposure to light:

0·1612 gave 7·2 c.c. N_2 at 21° and 754 mm. N=5·07.
$C_{17}H_{19}O_3N$ requires N=4·91 per cent.

The substance is freely soluble in organic media, including cold petroleum, although it may be crystallised from very concentrated hot solutions in this liquid; a solution containing 0·2613 gram in chloroform, made up to 25 c.c., gave α_D −2°43′ in a 2-dcm. tube, whence $[\alpha]_D$ −130·0°. On adding aqueous sodium hydroxide to the very pale yellow solution in alcohol, an intense yellow coloration is developed immediately, indicating very rapid hydrolysis.

The O-*methyl ether* was produced on agitating a solution of the compound in 10 per cent. sodium hydroxide with methyl sulphate, 2·4 grams being obtained from 3 grams; it is a bright yellow substance, crystallising from diluted methyl alcohol in thin, lustrous, yellow plates or transparent prisms, melting at 77°:

0·2399 gave 15·1 c.c. N_2 at 22° and 767·4 mm. N = 7·24.
$C_{11}H_{17}O_2N$ requires N = 7·18 per cent.

The compound dissolves very freely in cold methyl alcohol or petroleum; a solution containing 0·2616 gram in chloroform, made up to 25 c.c., gave α_D $-3°38'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-173·6°$. Hydrolysis does not take place with cold alcoholic alkali, but on heating during two hours under reflux and evaporating to small bulk, the characteristic, lustrous leaflets of sodium β-camphornitrilate separate; the acid from this source melted at 109° after recrystallisation from hot petroleum.

The *phenylurethane*,  $C_8H_{14}\left<\begin{array}{l}CO\\ \,|\\ C{:}NO\cdot CO\cdot NH\cdot C_6H_5\end{array}\right.$, was obtained without difficulty, separating from dilute methyl alcohol in small, pale yellow prisms or needles, melting and evolving gas at 118°:

0·2061 gave 16·9 c.c. N_2 at 23° and 766 mm. N = 9·37.
$C_{17}H_{20}O_3N_2$ requires N = 9·33 per cent.

The substance becomes brown on exposure to light. A solution containing 0·2565 gram in chloroform, made up to 25 c.c., gave α_D $-2°33'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-124·3°$, and this did not change when the liquid was protected from light during one week.

α-iso*Nitrosoepicamphor*.—The melting-point of the *iso*nitroso-compound from the β-oxime of phenyliminocamphor depends to some extent on the rate at which the temperature rises, and if this is slow, is apt to be indefinite; moreover, on heating the clear liquid still higher it becomes semi-solid, the product ultimately melting indefinitely above 160°. This is due to isomeric change into the less readily fusible modification, which is more conveniently prepared by boiling an aqueous solution of the β-*iso*nitroso-compound, and this transformation is facilitated by the presence of animal charcoal. Five grams of the β-form dissolved readily in 250 c.c. of boiling water, from which fern-like aggregates of unchanged material separated slowly on cooling, although the liquid was boiled vigorously during ten minutes; on redissolving this in the mother liquor, adding charcoal, and boiling during two or three minutes, the liquid began to deposit crystals as soon as it was filtered, and long, flat, silky needles separated, melting at 170°:

0·1285 gave 9·1 c.c. N_2 at 24° and 759·4 mm. N = 7·99.
$C_{10}H_{15}O_2N$ requires N = 7·74 per cent.

This modification dissolves in petroleum much less readily than the foregoing one (1:950). A solution containing 0·2550 gram in chloroform, made up to 25 c.c., gave α_D $-4°5'$ in a 2-dcm. tube, whence $[\alpha]_D$ −200·1°, falling to −196·0° in the course of four weeks.

The *benzoyl* derivative gave some difficulty in preparation. When produced by the pyridine method it remained oily after continued washing, and on treatment with very dilute acetic acid to remove adherent pyridine, it quickly underwent hydrolysis, the original α-*iso*nitrosoepicamphor being recovered. Moreover, on proceeding to shake an alkaline solution with benzoyl chloride, the colourless solid precipitated whilst the liquid was still bright yellow remained viscous when agitated with excess of benzoyl chloride. On using a deficit of the latter, however, and washing the solid product several times with cold petroleum, followed by recrystallisation from benzene diluted with the same volume of petroleum, snow-white leaflets were deposited, melting at 122·5°:

0·3474 gave 15·2 c.c. N_2 at 19° and 773 mm. N=5·13.
$C_{17}H_{19}O_3N$ requires N=4·91 per cent.

The substance is freely soluble in benzene or chloroform, but only slightly so in hot petroleum or cold alcohol; a solution containing 0·2590 gram in chloroform, made up to 25 c.c., gave α_D −2°40′ in a 2-dcm. tube, whence $[\alpha]_D$ −128·7°. The alcoholic solution becomes yellow immediately on adding alkali, indicating very rapid hydrolysis.

The O-*methyl* ether was produced in minor proportion on agitating an alkaline solution with methyl sulphate, the major product being the *N*-methyl ether of *iso*nitrosoepicamphor; after drainage from the latter, which is a pale yellow oil, the *O*-methyl derivative was recrystallised twice from hot petroleum, separating in lustrous, flat needles or massive, colourless, transparent prisms, melting at 100°:

0·2035 gave 13·0 c.c. N_2 at 23° and 772 mm. N=7·36.
$C_{11}H_{17}O_2N$ requires N=7·18 per cent.

A solution containing 0·2636 gram in chloroform, made up to 25 c.c., gave α_D −4°15′ in a 2-dcm. tube, whence $[\alpha]_D$ −201·5°.

The *N*-methyl ether of *iso*nitrosoepicamphor, drained from the *O*-ether as indicated above, dissolved readily in hydrochloric acid, and developed an intense yellow colour when heated with it; on diluting and extracting with ether the latter contained camphorquinone, whilst the presence of β-methylhydroxylamine in the acid liquid was indicated by reduction of Fehling's solution; thus the behaviour of the *N*-methyl ether resembles exactly that of the corresponding product from *iso*nitrosocamphor (Trans., 1904, **85**, 896).

The *phenylurethane*, purified with difficulty, was finally obtained in minute, colourless needles melting at 106° after being several times recrystallised from dilute alcohol; it evolved gas at the melting point, and became brown on exposure to light:

0·1287 gave 10·9 c.c. N_2 at 22° and 752 mm. N=9·54.

$C_{17}H_{20}O_3N_2$ requires N=9·33 per cent.

The substance is readily soluble in cold alcohol, but only sparingly so in benzene, and is insoluble in petroleum. A solution containing 0·0586 gram in chloroform, made up to 25 c.c., gave α_D −0°31′ in a 2-dcm. tube, whence $[\alpha]_D$ −110·2°.

*Spontaneous Decomposition of Benzoyl*iso*nitrosoepicamphor.*

A specimen of the yellow benzoyl derivative (m. p. 80°) from β-*iso*nitrosoepicamphor became oily and colourless after a few days in the desiccator, remaining in this condition during six weeks. The butter-like mass had acquired a faint odour of benzoic acid, and was rubbed with a cold aqueous solution of sodium carbonate, which extracted benzoic acid and left a colourless solid. This was recrystallised twice from hot benzene, separating in snow-white needles melting at 182°:

0·1673 gave 12·1 c.c. N_2 at 20° and 766 mm. N=8·37.

$C_{20}H_{28}O_3N_2$ requires N=8·14 per cent.

This result, coupled with the fact that it yielded β-camphornitrilic acid on hydrolysis, showed it to be the anhydride of that acid. The substance was sparingly soluble in cold benzene or alcohol, and insoluble in petroleum, whilst boiling alcohol dissolved it slowly, and deposited long, lustrous needles on cooling. A solution containing 0·2542 gram in chloroform, made up to 25 c.c., gave α_D 1°4′ in a 2-dcm. tube, whence $[\alpha]_D$ 52·4°.

Action of Hydroxylamine on the iso*Nitroso-derivatives of Epicamphor.*

The conversion of the new monoximes of camphorquinone into the dioximes proceeds much more rapidly than the corresponding transformation of *iso*nitrosocamphor. Two grams of the β-oxime dissolved in 10 c.c. of alcohol gave 1 gram of dioxime within half-an-hour of admixture with 1 gram of hydroxylamine hydrochloride and 2 grams of sodium acetate dissolved in 10 c.c. of water. Recrystallisation from hot ethyl acetate gave transparent prisms melting at 194° with vigorous effervescence, and yielding the characteristic chocolate precipitate on adding ferrous sulphate to a solution in very dilute alkali; 0·2630 gram dissolved in alcohol, made up to 25 c.c., gave α_D 1°42′ in a 2-dcm. tube, whence

$[\alpha]_D$ 80·8°; thus it is the δ-dioxime which is produced from this source, and that this is the sole product appears from the fact that the crop which followed the first gave $[\alpha]_D$ 80·5° without recrystallisation.

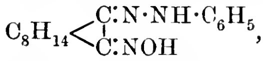
On treating the α-oxime in the same way, massive, transparent crystals melting at 224° separated (80 per cent.), the second crop melting at 242° and giving $[\alpha]_D$ −31·1° in 2 per cent. sodium hydroxide; this fraction was therefore nearly pure β-dioxime, and the first fraction, having $[\alpha]_D$ −60·3°, appeared to be a mixture of α- and β-dioximes. It was accordingly reprecipitated with dilute acid, shaken when dry with sufficient cold alcohol to dissolve the more soluble material, and filtered from the very sparingly soluble β-dioxime; the latter crystallised from boiling alcohol in brilliant prisms having $[\alpha]_D$ −24·5° (instead of −24·1°) in 2 per cent. sodium hydroxide, whence it may be concluded that the principal product is the β-dioxime, mixed with a small proportion of the α-modification.

Action of Phenylhydrazine on the iso*Nitroso-derivatives of Epicamphor.*

Whilst camphorquinonephenylhydrazone is converted into the oxime only with great difficulty, it being necessary to leave the pyridine solution containing free hydroxylamine during two months at 40—50° before transformation is complete (Trans., 1909, **95**, 955), the new monoximes of camphorquinone undergo condensation with phenylhydrazine very rapidly.

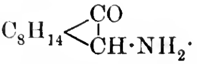
A solution of the α-oxime (0·5 gram) in 10 c.c. of absolute alcohol, when mixed with phenylhydrazine hydrochloride (0·5 gram) and sodium acetate (1 gram) in 5 c.c. of water, began to crystallise after three hours at air-temperature; after forty-eight hours there was collected 0·45 gram of transparent, rectangular, pale yellow prisms, melting at 197°, and not depressing the melting point of the known oxime of camphorquinonephenylhydrazone. Nevertheless, a solution of the recrystallised material containing 0·2847 gram in alcohol diluted to 25 c.c. gave α_D 6°17′ in a 2-dcm. tube, whence $[\alpha]_D$ 275·9°; in the course of five weeks this had fallen to $[\alpha]_D$ 142°, indicating complete transformation into the already known oxime of camphorquinonephenylhydrazone, which has $[\alpha]_D$ 147° in the same solvent. In chloroform the solution of the substance was colourless when freshly prepared, having $[\alpha]_D$ 259·2°, but the liquid rapidly became deep cherry-red, even when preserved in darkness, and did not transmit sufficient light for an observation in a 1-dcm. tube. The solution in concentrated sulphuric acid is intensely red, becoming practically colourless on adding a few drops of concentrated nitric acid.

When the β-monoxime was treated in exactly the same way, long, flattened, colourless needles separated within half-an-hour of mixing the solutions, and after five hours 0·68 gram was collected. Although quite different in appearance, the substance melted at the same temperature, and gave $[\alpha]_D$ 273·2° in alcohol and 260·8° in chloroform; moreover, these solutions behaved in exactly the same way as those prepared from the pale yellow prisms, the chloroform becoming too red for an observation, whilst the alcoholic liquid gave $[\alpha]_D$ 166·4° after three weeks, and became constant at 144° five weeks after the substance was dissolved, the solution having been preserved in darkness throughout this period.

It must be concluded, therefore, that phenylhydrazine converts the two new oximes into a new *camphorquinonephenylhydrazoneoxime*,  $C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot C_6H_5\\ |\\ C{:}NOH\end{matrix}$, identical from both sources, but dimorphous. In this connexion it may be recalled that the phenylhydrazone of *iso*nitrosocamphor occurred in two modifications, having $[\alpha]_D$ −235·5° and −139·5° respectively; here, also, the more highly rotatory form changed into the isomeride.

Action of Potassium Ferricyanide on iso*Nitrosoepicamphor.*

Five grams of the β-derivative dissolved in 50 c.c. of water containing 7·5 grams of potassium hydroxide, when treated with 12·5 grams of potassium ferricyanide in 50 c.c. of water, gave immediately a bulky, yellow precipitate, no doubt corresponding with the peroxide obtained from *iso*nitrosocamphor in similar circumstances (Trans., 1904, **85**, 899); in the course of two hours this had passed into solution, when dilute sulphuric acid precipitated an oil. On shaking the ethereal extract with aqueous sodium carbonate, the latter was transformed into a paste of lustrous leaflets, the sodium salt of β-camphornitrilic acid; the acid itself melted at 109°.

Aminoepicamphor,  $C_8H_{14}<\begin{matrix}CO\\ |\\ CH\cdot NH_2\end{matrix}$.

Six grams of β-*iso*nitrosoepicamphor dissolved in 40 c.c. of 20 per cent. sodium hydroxide was vigorously shaken with 7·5 grams of zinc dust added in small portions, the oily substance which was first precipitated disappearing on continued agitation; on extracting four times with ether, drying with sodium sulphate, and removing the solvent in a vacuum desiccator, 5 grams of crude material were deposited. As aminoepicamphor changes into epidihydrodicamphenepyrazine very rapidly, the recrystallisation must be carried out as soon as possible; using a small proportion of petroleum (b. p. 60—80°), colourless, fern-like crystals were produced, melting at 168—169°:

0·1908 gave 0·5013 CO_2 and 0·1746 H_2O. C=71·66; H=10·24.
0·1743 „ 12·8 c.c. N_2 at 21° and 771 mm. N=8·53.
$C_{10}H_{17}ON$ requires C=71·80; H=10·25; N=8·38 per cent.

Aminoepicamphor is freely soluble in organic media and also in water; it has an odour recalling that of bornylamine, but much fainter, and, although volatile in steam, it does not condense in a camphor-like mass on the side of a tube in the manner which characterises bornylamine. Like aminocamphor, the base reduces Fehling's solution when this is heated. A solution containing 0·2631 gram in absolute alcohol, made up to 25 c.c., gave α_D 0°15′ in a 2-dcm. tube, whence $[\alpha]_D$ 11·9°.

On reducing *α-iso*nitrosoepicamphor under the same conditions, the same aminoepicamphor is obtained.

The *hydrochloride*, precipitated by hydrogen chloride from a solution of the base in dry ether, was purified by adding ether to an alcoholic solution of the salt, when a gelatinous mass of snow-white, silky needles separated:

0·2148 gave 0·1507 AgCl. Cl=17·36.
$C_{10}H_{18}ONCl$ requires Cl=17·42 per cent.

It does not melt below 250°, above which temperature it decomposes.

The *platinichloride* crystallises in reddish-yellow needles on adding ether to the alcoholic solution, being freely soluble in alcohol and water; it melts and decomposes at 222°:

0·0748 gave 0·0195 Pt. Pt=26·07.
$(C_{10}H_{17}ON)_2H_2PtCl_6$ requires Pt=26·21 per cent.

The *picrate*, being freely soluble in alcohol, crystallises slowly in needles on adding water, and is therefore best prepared by mixing ethereal solutions of picric acid and of the base; it crystallises in stellate aggregates of primrose needles, melting and decomposing at 183°:

0·1287 gave 16·2 c.c. N_2 at 23° and 763·3 mm. N=14·32.
$C_{16}H_{20}O_8N_4$ requires N=14·14 per cent.

The *benzoyl* derivative, although somewhat viscid when prepared by the Schotten-Baumann process, became solid on being rubbed with cold petroleum; recrystallisation from hot petroleum, followed by a mixture of benzene and petroleum, gave colourless, transparent prisms melting at 144°:

0·1513 gave 7·0 c.c. N_2 at 22° and 762 mm. N = 5·28.

$C_{17}H_{21}O_2N$ requires N = 5·17 per cent.

A solution containing 0·3528 gram in chloroform, made up to 25 c.c., gave α_D $-0°41'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-24·2°$.

The *benzylidene* derivative separated in large, colourless, monoclinic prisms from a solution containing the factors; it melts at 84° after recrystallisation from dilute alcohol:

0·2974 gave 14·9 c.c. N_2 at 23° and 758·3 mm. N = 5·66.

$C_{17}H_{21}ON$ requires N = 5·49 per cent.

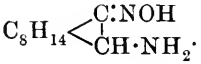
A solution containing 0·1026 gram in chloroform, made up to 25 c.c., gave α_D 2°27′ in a 2-dcm. tube, whence $[\alpha]_D$ 298·5°.

The *phenylcarbamide*, prepared in dry benzene, was precipitated by petroleum and recrystallised from dilute methyl alcohol, forming colourless, silky needles, melting at 181°:

0·1774 gave 15·2 c.c. N_2 at 22° and 771·5 mm. N = 9·90.

$C_{17}H_{22}O_2N_2$ requires N = 9·79 per cent.

A solution containing 0·2582 gram in chloroform, made up to 25 c.c., gave α_D 0°44′ in a 2-dcm. tube, whence $[\alpha]_D$ 35·5°.



Aminoepicamphoroxime, $C_8H_{14}<\begin{matrix}C:NOH\\ |\\ CH\cdot NH_2\end{matrix}$.

Contrasted with α-aminocamphor, aminoepicamphor is transformed very readily into the oxime. Five grams of the base, 4·2 grams of hydroxylamine hydrochloride, and 8·5 grams of crystallised sodium acetate dissolved in water, yielded with sodium carbonate 4·2 grams of colourless product after twelve hours at air-temperature. Recrystallisation from hot benzene or boiling water gave lustrous leaflets melting at about 115°; the substance then evolves gas, afterwards becomes solid, melting again at about 140°:

0·1085 gave 0·2496 CO_2 and 0·0988 H_2O. C = 62·74; H = 10·19.
0·1356 „ 17·4 c.c. N_2 at 20° and 764·5 mm. N = 14·83.

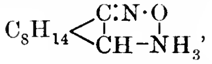
$C_{10}H_{18}ON_2$ requires C = 65·88; H = 9·96; N = 15·38 per cent.
$C_{10}H_{18}ON_2,\frac{1}{2}H_2O$ „ C = 62·77; H = 10·02; N = 14·66 per cent.

The substance does not undergo any alteration of melting point or composition when exposed in a desiccator containing calcium chloride, but with phosphoric oxide the lustre disappears within forty-eight hours, the white powder ultimately melting at 153°:

0·1110 gave 15·1 c.c. N_2 at 22° and 763 mm. N = 15·55.

$C_{10}H_{18}ON_2$ requires N = 15·38 per cent.

The anhydrous oxime appears to be optically inactive, but a solution of the hydrated form, containing 0·3120 gram in chloroform, made up to 25 c.c., gave α_D −0°30′ in a 2-dcm. tube, whence $[\alpha]_D$ −20·0°. This difference suggests a difference in structure, and may possibly be due to the formation of an internal salt,



$$C_8H_{14}<\begin{array}{l} C{:}N{\cdot}O \\ |\qquad | \\ CH{-}NH_3 \end{array},$$

because aminoepicamphoroxime, like the oxime of α-aminocamphor itself, is amphoteric.

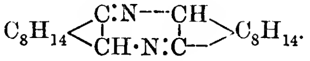
The *dibenzoyl* derivative, prepared from benzoyl chloride and the alkaline solution, was recrystallised four times from diluted methyl alcohol before a constant melting point was reached at 184°; it forms lustrous, hexagonal prisms, and although insoluble in petroleum, dissolves freely in alcohol or hot benzene:

0·1840 gave 11·6 c.c. N_2 at 21° and 766·6 mm. N = 7·27.

$C_{24}H_{26}O_3N_2$ requires N = 7·18 per cent.

A solution containing 0·2430 gram in chloroform, made up to 25 c.c., gave α_D −0°43′ in a 2-dcm. tube, whence $[\alpha]_D$ −36·8°.

Epidihydrodicamphenepyrazine,



$$C_8H_{14}<\begin{array}{l} C{:}N{-}{-}CH \\ |\qquad\quad | \\ CH{\cdot}N{:}C{-}{-} \end{array}>C_8H_{14}.$$

Even aminoepicamphor which has been carefully purified becomes pale brown during a few hours in the desiccator, and after fifteen hours a specimen which had given C = 71·66 per cent. on the day of preparation gave C = 72·69 per cent., whilst the percentage of nitrogen gradually rose with lapse of time from 8·4 to 9·3 ($C_{20}H_{30}N_2$ requires N = 9·39 per cent.). The condensation may be hastened without detriment to the product by maintaining a temperature of about 50° during fifteen to twenty hours; on dissolution in dilute sulphuric acid, ether removed a small proportion of camphorquinone, whilst sodium hydroxide precipitated from the acid a specimen of epidihydrodicamphenepyrazine which required to be recrystallised from diluted alcohol three or more times before the melting point became constant at 163°:

0·1640 gave 0·4833 CO_2 and 0·1503 H_2O. C = 80·37; H = 10·26.

$C_{20}H_{30}N_2$ requires C = 80·47; H = 10·13 per cent.

From this it will appear that the auto-condensation of aminoepicamphor proceeds far more rapidly than the corresponding alteration of α-aminocamphor; its completion can be at once recognised by the indifference of the product towards Fehling's solution. Unlike aminoepicamphor, it is insoluble in water, although dissolving readily in mineral acids and organic media, including petroleum. A solution containing 0·2605 gram in chloroform, made up to 25 c.c., gave α_D 8°52′ in a 2-dcm. tube, whence $[\alpha]_D$ 425·5°, and we think the magnitude of the specific rotatory power, in view of the facility with which the substance is produced from aminoepicamphor, explains the discrepancy between the rotation of the latter base recorded by Bredt and Perkin (30·15°) and our own observation (11·9°). A solution containing 0·2618 gram of the dihydrodicamphenepyrazine from α-aminocamphor under similar conditions gave α_D $-5°56'$, whence $[\alpha]_D$ $-283·3°$.

The *picrate* separates from an alcoholic solution of the base and picric acid only on dilution with water, and crystallises from ether in massive prisms; when recrystallised from dilute alcohol it forms canary-yellow, dagger-shaped leaflets, melting at 177°:

0·0899 gave 11·6 c.c. N_2 at 22° and 757 mm. N=14·62.

$C_{32}H_{36}O_{14}N_8$ requires N=14·82 per cent.

Thus the salt contains picric acid in the molecular proportion of two to one. It is insoluble in cold water, and freely soluble in alcohol; a solution containing 0·1229 gram in this solvent, made up to 25 c.c., gave α_D 2°28′ in a 2-dcm. tube, whence $[\alpha]_D$ 250·9°. The addition of picric acid has therefore enhanced the activity of epidihydrodicamphenepyrazine, for whilst the latter has $[M]_D$ 1268°, that of the picrate is 1896°.

The *hydrochloride*, precipitated from an ethereal solution of the base by hydrogen chloride, melts and decomposes above 260°:

0·0765 gave 0·0583 AgCl. Cl=18·85.

$C_{20}H_{30}N_2,2HCl$ requires Cl=19·11 per cent.

The salt dissolves freely in water or alcohol, undergoing incomplete hydrolysis.

As already explained, epidihydrodicamphenepyrazine is isomeric with the dihydrodicamphenepyrazine of Duden and Pritzkow, but should yield the same dicamphenepyrazine on oxidation, whatever view is taken of the constitution of the latter substance. On warming a solution of epidihydrodicamphenepyrazine in dilute hydrochloric acid with ferric chloride, the liquid became turbid, and there separated an oil which solidified when cold; recrystallisation twice from dilute alcohol gave colourless, refractive prisms, melting at 159°, not depressed by admixture with dicamphenepyrazine from α-aminocamphor. A solution containing 0·2550 gram in chloroform, made up to 25 c.c., gave α_D 1°8′ in a 2-dcm. tube, whence $[\alpha]_D$ 55·5°.

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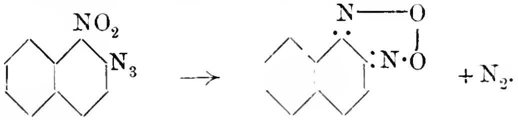
CXLIII.—*The Triazo-group. Part XXI. Benzenoid Azoimides Containing Multivalent Iodine.*

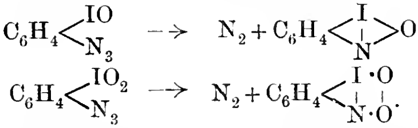
By Martin Onslow Forster and Johannes Heinrich Schaeppi.

In the course of a communication on the nitronaphthylazoimides (Trans., 1907, **91**, 1942) attention was drawn to the facility with which 1-nitro-2-naphthylazoimide loses nitrogen, yielding quantitatively the peroxide of β-naphthaquinonedioxime:



o-Nitrophenylazoimide gradually undergoes a similar change at common temperatures, producing the so-called *o*-dinitrosobenzene or, more properly, the peroxide of *o*-benzoquinonedioxime.

It was therefore natural to inquire whether the neighbourhood of an iodoso- or iodoxy-group might not lead to a corresponding disintegration of the azoimide nucleus, followed by some association between iodine and nitrogen, as, for example, the following:



$$C_6H_4<\begin{matrix}IO\\N_3\end{matrix} \rightarrow N_2 + C_6H_4<\begin{matrix}I\\|\\N\end{matrix}>O\ ;$$

$$C_6H_4<\begin{matrix}IO_2\\N_3\end{matrix} \rightarrow N_2 + C_6H_4<\begin{matrix}I\cdot O\\| \quad |\\N\cdot O\end{matrix}.$$

Accordingly, we have prepared the three iodophenylazoimides and their respective triazophenyliodochlorides, triazoiodosobenzenes, triazoiodoxybenzenes, and di-triazophenyliodinium iodides, with the prospect that either 1:2-triazoiodosobenzene or 1:2-triazoiodoxybenzene might undergo the alteration indicated. In these compounds, however, the triazo-group appears to be very stable, so that the iodoso-derivative leads in the ordinary way to the iodoxy-compound by continued heating:

$$2N_3\cdot C_6H_4\cdot IO = N_3\cdot C_6H_4I + N_3\cdot C_6H_4\cdot IO_2.$$

Furthermore, the 1:2-triazoiodoxybenzene produced in this manner, like the meta- and para-derivatives, is very explosive, detonating violently when rubbed or struck, so that it was not possible to recognise any product of its milder transformation.

Although from the original point of view the investigation of these materials proved fruitless, certain matters in connexion with them appear to be worthy of record. In the first place, their very existence is somewhat significant in view of the suggestion by Thiele that hydrazoic acid and organic azoimides should be represented by the formula X·N⁚N⁚N, instead of by the more conventional cycloid (*Ber.*, 1911, **44**, 2522). It is difficult to believe that such an arrangement of unprotected nitrogen atoms would not undergo disruption by chlorine, or at least take up two atomic proportions of the halogen as a prelude to such disruption. It is still less conceivable that such a complex, finding itself in the ortho-position as to groups so active as the iodoso- and iodoxy-radicles, would not take part in some combination or disintegration. So far is this from being the case, however, that the iodophenylazoimides may be carried through the complete series of changes to the di-triazophenyliodinium salts without suffering any alteration of the azoimide nucleus:

$$N_3 \cdot C_6H_4I \longrightarrow N_3 \cdot C_6H_4 \cdot ICl_2 \longrightarrow N_3 \cdot C_6H_4 \cdot IO \longrightarrow$$
$$N_3 \cdot C_6H_4 \cdot IO_2 \longrightarrow (N_3 \cdot C_6H_4)_2I \cdot I.$$

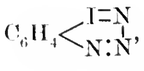
In one respect the *o*-triazoiodosobenzene distinguishes itself from the isomerides. Specimens which had been preserved in darkness during some weeks were found to have changed into di-*o*-triazophenyliodinium salt, although the normal course of spontaneous change in iodosobenzene derivatives appears to be that described by Willgerodt (*Ber.*, 1894, **27**, 1826), who noted the formation of the iodoxy-compound from iodosobenzene, as well as from the *m*-nitro-, *o*-chloro-, and *p*-bromo-derivatives. The iodinium salt produced in this manner is probably the iodate, because on removing the regenerated 1:2-triazoiodobenzene and pouring an acetic acid solution of the residue into sodium thiosulphate, di-*o*-triazophenyliodinium iodide was precipitated, suggesting the following changes as having occurred spontaneously:

$$2N_3 \cdot C_6H_4 \cdot IO = N_3 \cdot C_6H_4I + N_3 \cdot C_6H_4 \cdot IO_2.$$
$$N_3 \cdot C_6H_4 \cdot IO + N_3 \cdot C_6H_4 \cdot IO_2 = (N_3 \cdot C_6H_4)_2I \cdot IO_3.$$

It should be stated, however, that 1:2-triazoiodosobenzene, as produced from the iodochloride by alkali, assumes an unusually pulpy form, and as it cannot be recrystallised, the associated alkali is extremely difficult to remove; it is just possible, therefore, that the above change is induced by traces of alkali remaining in the substance.

In attempting to follow the spontaneous alteration incurred by *o*-triazoiodosobenzene, we did not immediately recognise the iodinium salt as such, the possibility of the product having the constitutional formula,

$$N_3 \cdot C_6H_4I{:}I \cdot C_6H_4 \cdot N_3 \quad \text{or}$$



$$C_6H_4 \lessdot \begin{matrix} I = N \\ | \\ N{:}N \end{matrix},$$

being still kept in mind. Chlorine was therefore allowed to act on it, in the expectation that the former expression would lead to *o*-triazophenyl iodochloride, whilst the alternative molecule would lose nitrogen. The actual result was a bright yellow substance resembling the iodochloride in appearance, and having the same composition as that derivative, but ultimately recognised as the tetrachloride of di-*o*-triazophenyliodinium iodide. In order to ascertain what had actually occurred, we carried out the same experiment with the less complex diphenyliodinium iodide itself, and this led to the discovery of the perhalides of that salt recently described (this vol., p. 382).

In conclusion, it has to be noted that the three iodophenylazoimides are unexpectedly resistant towards alcoholic alkali, which leaves the triazo-group intact and eliminates only traces of iodine during many hours.

EXPERIMENTAL.

The Iodophenylazoimides, $N_3 \cdot C_6H_4I$.

Ten grams of the iodoaniline suspended in 200 c.c. of water mixed with 30 c.c. of sulphuric acid were diazotised with 3·5 grams of sodium nitrite; carbamide having been added in quantity sufficient to destroy free nitrous acid, the ice-cold liquid was poured into 100 c.c. of water containing 3·5 grams of sodium azide, when vigorous liberation of nitrogen took place. The azoimide was then extracted with ether.

1:2-*Triazoiodobenzene* is a colourless oil, which rapidly becomes brown on exposure to light:

0·2702 gave 40·9 c.c. N_2 at 25° and 771 mm. N = 17·35.

$C_6H_4N_3I$ requires N = 17·15 per cent.

The substance boils at 90—91°/0·9 mm., and has an intensely pungent odour. Continued heating with alcoholic alkali fails to remove the triazo-group, and only a trace of iodine was noticeable after six hours.

1:3-*Triazoiodobenzene* is also liquid, and although colourless when freshly prepared, rapidly becomes pale yellow when exposed to light:

0·1621 gave 24·7 c.c. N_2 at 23° and 763 mm. N = 17·34.

It boils at 82—83°/0·85 mm., and has a faint odour recalling that of ethoxynaphthalene, but becoming pungent and acidic with steam.

1:4-*Triazoiodobenzene* solidified on evaporating the ether, and was recrystallised from hot absolute alcohol, which deposited pale yellow plates melting at 36°:

0·1873 gave 27·9 c.c. N_2 at 23° and 777 mm. N = 17·27.

The substance is extremely sensitive towards light, and should be prepared in a darkened room, as otherwise it is coloured brown; it has an agreeable odour recalling anise. Chloroform, alcohol, ether, or benzene dissolve it very readily, but it is somewhat less soluble in petroleum and glacial acetic acid. Boiling alcoholic alkali does not remove the triazo-group, and the proportion of iodine eliminated after eight hours is trifling.

The Triazophenyliodochlorides, $N_3 \cdot C_6H_4 \cdot ICl_2$.

Dry chlorine was passed into 25 c.c. of chloroform containing 5 grams of the iodophenylazoimide, rise of temperature being checked by external cooling; after ten minutes the yellow, crystalline product was filtered, the mother liquor yielding a further quantity on evaporation.

1-*Triazophenyl* 2-*iodochloride* is almost completely precipitated in bright yellow crystals which are extremely unstable, dark patches beginning to appear after a few hours; if preserved in a stoppered bottle, the decomposition is completed in the course of one night:

0·2041 gave 22·9 c.c. N_2 at 24° and 774 mm. N = 12·95.

$C_6H_4N_3Cl_2I$ requires N = 13·29 per cent.

1-*Triazophenyl* 3-*iodochloride* separated from the chloroform in slender needles much paler in colour than the ortho-compound; it began to lose chlorine at about 85—90°, and underwent decomposition with partial fusion at 105—110°:

0·1790 gave 21·0 c.c. N_2 at 22° and 765 mm. N = 13·43.

It resembles the foregoing substance in the profound change which it undergoes when preserved in an enclosed vessel, but the alteration, which involves liberation of iodine, does not take place so rapidly.

1-*Triazophenyl* 4-*iodochloride* crystallises in small pyramids, and begins to decompose at about 90—95°, losing chlorine; the change becomes more profound at 105°, when the substance darkens and undergoes complete fusion:

0·2283 gave 27·0 c.c. N_2 at 21° and 770 mm. N = 13·58.

0·2767 required 17·0 c.c. *N*/10-sodium thiosulphate. Cl = 21·70.

$C_6H_4N_3Cl_2I$ requires N = 13·29; Cl = 22·49 per cent.

The substance is very unstable, becoming black and viscid during a few days in the desiccator, in which the vapour of iodine is soon noticeable.

The Triazoiodosobenzenes, $N_3 \cdot C_6H_4 \cdot IO$.

Ten grams of the iodochloride were shaken with 100 c.c. of 5 per cent. aqueous sodium hydroxide during two to three hours; this destroyed the intense yellow colour, producing a faint yellow, amorphous material, which was washed thoroughly with water, as it was not possible to recrystallise the product.

1:2-*Triazoiodosobenzene* was formed more rapidly than the isomerides, separating in a condition so pulpy that it was impossible to free it completely from alkali; for the same reason it was difficult to remove the last traces of moisture. There is not a definite melting point, the substance becoming soft at about 85°, and melting, with liberation of gas, at 90—100°; the product does not explode, even when heated to 160°.

The *acetate*, $C_6H_4N_3I(C_2H_3O_2)_2$, obtained by dissolving the freshly prepared iodoso-compound in glacial acetic acid, was recrystallised from benzene, and melted at 155—157°:

0·2350 gave 24·2 c.c. N_2 at 27° and 763 mm. $N = 11·53$.
0·2846 „ 0·1878 AgI. $I = 35·67$.
$C_{10}H_{10}O_4N_3I$ requires $N = 11·57$; $I = 35·00$ per cent.

The *chromate*, produced on adding aqueous chromic acid to the acetate dissolved in glacial acetic acid, separates as a brick-red precipitate, which suddenly liquefies and becomes quite dark.

1:3-*Triazoiodosobenzene* was filtered from the alkaline suspension after three hours, taking the form of a faint yellow, amorphous, somewhat pulpy material, less bulky than the ortho-iodoso-derivative, but still difficult to purify; it explodes at 125°.

The *acetate* was crystallised from benzene, and melted at 118—120°:

0·2402 gave 24·5 c.c. N_2 at 22° and 764 mm. $N = 11·68$.

The *chromate* was deep-red, and when separated from the liquid, changed spontaneously to a black mass and exploded feebly. The *nitrate* crystallised in lustrous, faint yellow needles when a solution of the acetate, treated with a few drops of nitric acid, was allowed to remain during several hours; it melted at 83—84°. The *formate* explodes at 78°, and must be precipitated with water very soon after the iodoso-compound is dissolved in formic acid, as otherwise meta-iodophenylazoimide is produced.

1:4-*Triazoiodosobenzene* was removed from the alkali after three hours' shaking, since more prolonged contact causes it to turn brown; it explodes violently when heated to 130° or when treated with concentrated nitric or sulphuric acid:

0·2228 gave 0·2005 AgI. $I = 49·76$.
$C_6H_4ON_3I$ requires $I = 48·66$ per cent.

When dissolved in glacial acetic acid and poured into a decinormal solution of sodium thiosulphate, the freshly prepared iodoso-compound is reduced to 1:4-triazoiodobenzene; this remark applies also to specimens which have been preserved in darkness during three months, thereby distinguishing this compound from the ortho-derivative. The substance rapidly becomes brown when exposed to light.

The *acetate* was recrystallised from benzene, and melted at 165—166° without decomposition:

0·1846 gave 18·6 c.c. N_2 at 24° and 766 mm. N = 11·46.
0·2487 „ 0·1634 AgI. I = 35·52.
$C_{10}H_{10}O_4N_3I$ requires N = 11·57; I = 35·00 per cent.

It dissolves in acetone, benzene, or alcohol, but is insoluble in water or petroleum.

The *chromate* is a deep-red substance insoluble in benzene and only sparingly soluble in water. It is a very dangerous material, as in the dry state it explodes when lightly rubbed; there is not a definite melting point, violent explosion occurring at about 71°.

The *nitrate*, $C_6H_4N_3I(NO_3)_2$, separating first as an oil on adding dilute nitric acid to the acetate dissolved in glacial acetic acid, is a bright yellow, crystalline substance, melting at 102° without decomposition:

0·1112 gave 17·9 c.c. N_2 at 26° and 760 mm. N = 18·37.
$C_6H_4O_6N_5I$ requires N = 18·97 per cent.

It is freely soluble in alcohol, acetone, chloroform, or glacial acetic acid, but is not dissolved by benzene, petroleum, or water.

The *formate* appears as an emulsion on adding water to a solution of the iodoso-compound in formic acid, but the salt ultimately crystallises in plates which explode at 85°. If water is not added very soon after dissolution, *p*-iodophenylazoimide is the only product.

Spontaneous Decomposition of 1:2-*Triazoiodosobenzene.*

Whilst the freshly prepared substance behaves towards sodium thiosulphate in the same manner as the isomerides, yielding 1:2-triazoiodobenzene, specimens which have been preserved in darkness during several weeks behave quite differently. In the first place, the dry substance when heated swells up considerably at 90—100°, and undergoes imperfect fusion at 160—162°. On pouring the glacial acetic acid solution of this material into sodium thiosulphate, there is precipitated a faint yellow solid, insoluble in acetic acid, benzene, or chloroform, and only very sparingly soluble in alcohol; it does not liberate iodine from potassium iodide, and it melts at 168°:

0·1362 gave 20·6 c.c. N_2 at 23° and 766 mm. N = 17·28.
0·3553 „ 0·3465 AgI. I = 52·70.
$C_6H_4N_3I$ requires N = 17·15; I = 51·84 per cent.

On passing chlorine into a suspension of the substance in chloroform a red coloration was produced, and ultimately the colourless, amorphous solid was transformed into the characteristic, yellow, crystalline tetrachloride of di-*o*-triazophenyliodinium iodide (see below), thus identifying the spontaneous transformation product from 1:2-triazoiodosobenzene as di-*o*-triazophenyliodinium iodide itself.

The Triazoiodoxybenzenes, $N_3 \cdot C_6H_4 \cdot IO_2$.

On passing a current of steam through an aqueous suspension of the triazoiodosobenzenes the corresponding triazoiodobenzene is carried over, and the residual liquid, when filtered and concentrated, yields the iodoxy-compound in crystalline form.

1:2-*Triazoiodoxybenzene* separates in pale brown needles, exploding violently at 157°:

0·2070 gave 0·1794 AgI. I = 45·66.

$C_6H_4O_2N_3I$ requires I = 45·85 per cent.

The dry substance is highly explosive, detonating violently when lightly rubbed or struck. It may be recrystallised from warm glacial acetic acid without undergoing change. On titration with sodium thiosulphate after adding potassium iodide to a solution in glacial acetic acid containing hydrochloric acid, abnormal results were obtained, the amount of iodine set free slightly exceeding one-half of that expected. Moreover, the product, instead of being 1:2-triazoiodobenzene, consisted of di-*o*-triazophenyliodinium iodide.

1:3-*Triazoiodoxybenzene* is not produced so readily as the foregoing substance; it crystallises in pale brown needles, exploding violently at 175—180°, and dissolves in water or glacial acetic acid.

1:4-*Triazoiodoxybenzene* forms colourless crystals, which rapidly become brown; it explodes violently at about 170°, and also when brought in contact with concentrated sulphuric acid, which produces a flame. Owing to its dangerous character no analyses were made, but a weighed quantity, when mixed with a solution of potassium iodide acidified with sulphuric and acetic acids, oxidised an amount of thiosulphate solution corresponding with 10·1 per cent. of available oxygen, $C_6H_4O_2N_3I$ requiring 11·5 per cent.

The Di-triazophenyliodinium Iodides, $(N_3 \cdot C_6H_4)_2I \cdot I$.

Molecular proportions of the triazoiodosobenzene and the triazoiodoxybenzene with the calculated amount of silver oxide were made into a paste with water and shaken during three to four hours. The filtered liquid having been saturated with sulphur dioxide was treated with potassium iodide, which precipitated a colourless solid.

*Di-*o*-triazophenyliodinium iodide* is practically insoluble in everything, and melts at 168°:

0·0891 gave 13·6 c.c. N_2 at 22° and 750 mm. N = 17·15.

$C_{12}H_8N_6I_2$ requires N = 17·15 per cent.

On adding aqueous chromic acid to the solution of iodinium hydroxide as filtered from the silver iodide, an orange-yellow precipitate of di-*o*-triazophenyliodinium chromate was produced, exploding at 165°.

*Di-*m*-triazophenyliodinium iodide* melts at 171°:

0·2084 gave 31·2 c.c. N_2 at 23° and 775 mm. N = 17·31.

In general behaviour and insolubility it resembles the isomeride.

*Di-*p*-triazodiphenyliodinium iodide* melts at 174°:

0·1245 gave 18·7 c.c. N_2 at 23° and 769 mm. N = 17·32.

*Action of Chlorine on Di-*o*-triazophenyliodinium Iodide.*

On passing chlorine into a chloroform suspension of the iodinium iodide, the liquid first acquired the appearance of a solution of iodine in chloroform, but gradually the dark colour faded to yellow; the suspended solid seemed grey, but with continued passage of the gas the final colour of crystals and liquid was bright yellow. The product liberated chlorine at about 80°, and decomposed at 105—110°:

0·1442 gave 17·6 c.c. N_2 at 24° and 758 mm. N = 13·66.

$C_{12}H_8N_6Cl_4I_2$ requires N = 13·30 per cent.

It is therefore the *tetrachloride* of di-*o*-triazophenyliodinium iodide. When treated with ordinary solvents it is found to be very sparingly soluble, becoming resolved by boiling benzene, for example, into *di-*o*-triazophenyliodinium chloride*:

0·1183 gave 22·3 c.c. N_2 at 24° and 751 mm. N = 21·06.

$C_{12}H_8N_6ClI$ requires N = 21·10 per cent.

This forms pale brown crystals melting at 191—192°; it is soluble in water, and yields the iodinium iodide with potassium iodide.

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CXLIV.—*The Formation of Neon as a Product of Radioactive Change.*

By Sir William Ramsay, K.C.B., F.R.S.

In 1908 (Trans., **98**, 993) Mr. Cameron and I described experiments in which niton was left in contact with water in a silica bulb; the gaseous products were hydrogen and oxygen, nitrogen, possibly carbon dioxide, and of the rare gases, helium and neon. It was then remarked that "it is extremely difficult to prevent traces of air leaking into the apparatus during the considerable length of time which must elapse before an experiment is completed"; consequently argon was also present in the gaseous mixture, and it was not certain whether its presence was due to the entry of air. Subsequently, Mr. Soddy pointed out that neon can be recognised in about 0·2 c.c. of air; and it appears to have been generally assumed that the neon found by us owed its presence to atmospheric contamination.

I have now other evidence which makes it almost certain that neon is either a product of degradation of niton, or produced by the action of niton on water; preferably the latter alternative. The evidence is (*a*) observational, and (*b*) experimental.

(*a*) *Observational Evidence.*—The mineral springs at Bath have a temperature of about 50°, and a considerable amount of gas bubbles through the water and escapes. From the King's Well the yield of gas in twenty-four hours is close on 5 cubic metres. This gas consists of carbon dioxide, 36 c.c., and nitrogen with inert gases, 964 c.c. per litre. There is no free oxygen; a special test for hydrogen was made by condensing in charcoal, cooled with liquid air, the carbon dioxide and the nitrogen from 432 c.c. of this gas. The uncondensed gases, mainly nitrogen and argon, were pumped off, and amounted to 3·406 c.c. On adding oxygen and sparking, there was no explosion, and no contraction was observed on remeasuring. Hence hydrogen was absent.

The natural gas is strongly radioactive; the niton it contains is in equilibrium with 33·65 milligrams of radium per million litres; or, in other words, a million litres of the gas contains about 1/3000th of a milligram of niton. The water is also radioactive; it actually contains radium to the amount of 0·139 milligram (taken as metal) in a million litres; and it is also saturated with niton, regard being had to the volume of the other gases. Details concerning this water are published in the following paper (p. 1370); but attention is now directed to the fact that it contains appreciable quantities of radium and niton.

The gas escaping from the King's Well contains per litre:

Argon, 7·263 c.c.; neon, 2·334 c.c.; and helium, 0·297 c.c.

Atmospheric air contains per litre:

Argon, 9·32 c.c.; neon, 0·124 c.c.; and helium, 0·00408 c.c.

The ratios are: $\frac{7{\cdot}263}{9{\cdot}320} = 0{\cdot}78$; $\frac{2{\cdot}334}{0{\cdot}0124} = 188$, and $\frac{0{\cdot}297}{0{\cdot}00408} = 73$; in fact, there is about three-quarters as much argon in the King's Well gas as in an equal volume of air; there is 188 times as much neon; and there is 73 times as much helium. The presence of helium can be accounted for by the disintegration of the subterranean radium and the niton, etc. Whence comes the neon?

(*b*) *Experimental Evidence.*—On August 2nd, 1910, a solution of thorium nitrate in about 5 c.c. of water from which gases had on four several occasions been pumped off, after treatment with varying doses of niton was sealed up. The extraction of such gases, of course, precluded the presence of air in the bulb containing the thorium solution. This solution had added to it at that date 0·1028 cubic millimetre of niton, as previously described (*loc. cit.*); and it remained sealed, without possible leakage, for more than two years; the niton, of course, had disintegrated. As each cubic millimetre of niton gives 3 cubic millimetres of helium, the total helium formed should have been 3 × 0·1028 or 0·3084 cubic millimetres, provided that none had entered the glass.

The gases were extracted, and after separation of carbon dioxide by leaving the gases in contact with fused slightly moist potassium hydroxide, melted on to the upper end of a tube, any adhering film of air in which had been removed by a preliminary "wash-out" with oxygen, the gas was exploded after addition of a little pure oxygen. The remainder, consisting of nitrogen (from the nitrate) and oxygen, was introduced into an apparatus connected with a small bulb containing charcoal which could be cooled with liquid air. This bulb had been previously jacketed with the vapour of boiling sulphur, and pumped empty by aid of a Töpler pump with a fall-tube of very narrow bore. It may be taken that practically all air was extracted from the charcoal.

Having introduced the residue of nitrogen and oxygen, the stopcock leading to the cooled charcoal bulb was opened. Rapid absorption took place, and the gases were kept in communication with the cooled charcoal for half an hour. The stopcock was then shut, and by raising a reservoir of mercury the remaining gas was forced up into a narrow calibrated capillary tube, provided with a platinum electrode at the top. It was then measured. As a mean of four measurements at different pressures, its volume was found to be 0·485 cubic millimetre.

The spectrum of this gas was next examined. The red and blue lines due to hydrogen were observed, but were weak. The helium spectrum was visible in its entirety, and was very bright; and the neon spectrum was also very strong. My colleague, Prof. Collie, estimated that from previous observations which he had frequently made of the relative intensity of the spectra of mixtures of helium and neon, the neon must have been present in quantity equal to one-third or one-fourth of that of the helium. My own impression was the same. Assuming the volume of the hydrogen to be negligible, then the volume of neon would be $0·485-0·308=0·177$ cubic millimetre. Judging from the brilliancy of the spectrum, this may not have been impossible. Even granting that the actual volume of the neon was not more than 0·05 cubic millimetre, that would have implied the leakage into the gas of no less than 4 c.c. of air.

The possibility of air having been present, however, was easily put to the test. By heating the charcoal-tube with the vapour of boiling sulphur, the residual gases in the charcoal were expelled into the apparatus, which had been thoroughly washed out with pure oxygen, and connexion was made with a small silica tube holding an iron boat containing some metallic lithium, from which gases had been completely extracted by heating it in a vacuum. The oxygen and the nitrogen were rapidly absorbed; the residual gas, of which scarcely any was present, gave no spectrum of argon, unless a jar and spark-gap were interposed; in that case it was just possible to see the blue lines. Now, had there been a leakage of a tenth of a c.c. of air, the argon should have measured 0·9 cubic millimetre, instead of an unmeasurable trace, and its spectrum should have been brilliant. It is safe, therefore, to conclude that the air-leakage was insignificant, and it follows that the neon must have been produced from the niton or by the niton.

An experiment was made with about 0·5 c.c. of air to ascertain the brilliancy of the spectrum of the neon which it contained, after condensing the condensable gases in cooled charcoal. This quantity of air should have contained 0·06 cubic millimetre of neon; the spectrum was comparable in brilliancy with, but not so brilliant as, that of the neon separated from the gases of the thorium solution.

It may be taken, therefore, that, as already stated in 1908, if niton decomposes in presence of water, that is, presumably, in solution, neon is produced. It might be a disintegration-product of niton, or it might be formed by the union of five atoms of helium, although the atom of neon weighs 20·2, whilst five atoms of helium together add to 19·97, giving a deficit of 0·23 unit; or, lastly, water may participate in the action, and its oxygen or hydrogen may play a part in the change.

In the experiments with the thorium solution the niton must have been partly in the liquid, partly in the gaseous phase. It would appear that the gaseous phase gives only helium; for the fact that neither thorium minerals nor uranium minerals give any neon mixed with the helium which can be extracted by solution or by heating, shows that in absence of water, helium is the only product. Again, the relatively large amount of neon in the gases from the King's Well would point to the disintegration of niton having occurred mainly in solution, for there is nearly eight times as much neon present in these gases as there is helium. One remarkable circumstance is the absence of free hydrogen and oxygen, which are the usual products when niton acts on water.

I have much pleasure in thanking Mr. Irvine Masson for assistance in determining the densities of the gaseous samples, thus giving the percentages of argon, neon, and helium.

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CXLV.—*An Analysis of the Waters of the Thermal Springs of Bath.*

By IRVINE MASSON, M.Sc., and SIR WILLIAM RAMSAY, K.C.B. F.R.S.

THE waters of Bath, *Aquae Solis*, have been used for drinking and bathing since the first centuries of our era. The Roman baths have been partly disinterred, and are to be seen lying some 15 or 20 feet below the present level of the soil. The waters have long been known for their therapeutic properties, and analyses of them have been carried out on several occasions. The temperature of the water is high—about 50° (116—120° F.), and from the springs gases bubble up in large quantity.

There are three main springs: that which feeds the King's Bath, celebrated in the eighteenth century and during the Regency as a resort of beauty and fashion; the Hetling Spring, from which the Pump-room Hotel and the large swimming-bath are fed; and the Cross Spring, which also feeds a swimming-bath open to the public. The first is by far the most copious in its supply; it is estimated to deliver over 500,000 gallons in twenty-four hours, most of which finds its way into the River Avon, after use in the various bathing establishments. From the King's Spring the celebrated Pump-room is fed; the water is forced up some 15 feet to a fountain, from which the attendants distribute it hot and steaming to the visitors.

The glasses from which they drink the water have been long in use, and it is noteworthy that they are stained yellow, as if with iron; but hydrochloric acid fails to remove the colour, which, indeed, penetrates the substance of the glass; it is due to the action of the niton contained in the water on the silicate, liberating metallic potassium in an atomic state of subdivision (see J. C. Maxwell Garnet, *Phil. Trans.*, 1906, *A*, **206**, 237). The glass is "crystal," a silicate of potassium and lead. Soda-glass, similarly exposed, turns pale violet, a colour not due to the presence of manganese, but to the modification of the light passing through the atomically subdivided sodium set free by the influence of niton, or radium emanation.

The water enters the Roman baths through pipes of lead of rectangular section, lapped, not soldered or drawn. This lead was found to contain 26·2 grams of silver per ton.

The density of the water is 1·0175 at 4°. It has a freezing point of $-0·07°$, corresponding with that of a solution of common salt containing 1·09 grams per litre. In terms of osmotic pressure the dissolved salts exert a pressure of 871 grams per sq. cm.

Analyses of the gases escaping from these waters have been made by Priestley ("On Air," Vol. II., p. 225, Ed. 1776), who found it to contain 1/20th of "fixed air," and that the remainder "was almost entirely noxious," that is, consisted of nitrogen; by Daubeny (*Phil. Trans.*, 1834, p. 1); and by Williamson (*Brit. Assoc. Report*, 1865, p. 380). Daubeny's results are very meagre; he found the carbon dioxide in the gas escaping from the King's Bath to vary between 45 and 135 parts per 1000; and the oxygen in the residue freed from carbon dioxide by potassium hydroxide was stated to be "rather less than 4 parts," and the nitrogen "rather more than 96 parts" per 100. Williamson made five analyses of the gases from the King's Bath; carbon dioxide varied from 27·21 to 35·11 c.c. per litre; oxygen from 0·19 to 0·62 c.c.; marsh gas on two occasions amounted to 0·18 and 2·61 c.c.; and nitrogen in the same two samples was 963·3 and 961·1 c.c. per litre.

In 1899 an analysis of the escaping gas was made at the "Lancet" Laboratory; the gases were collected from the Cross Spring. The results are variable; carbon dioxide fluctuated between 16 and 39·5 c.c. per litre; oxygen between 16 and 45·7 c.c.; nitrogen with inert gases between 914·8 and 968·0 c.c.; and the nitrogen contained argon and helium equal to 16·1 c.c. per litre.

Our samples were collected in the beginning of January, 1912, from the King's Well. A large funnel covers the opening, and is immersed in the water; from this funnel a pipe conducts the gas to a small gasometer; and from observations, for which we have to thank Mr. Jones, the Corporation's engineer, the volume of gas issuing from the King's Spring is no less than 174 cubic feet, or 4927 litres, in twenty-four hours. Cross Spring and Hetling Spring were estimated to yield 218 litres each in the same period of time. Altogether, the three springs give 3563 litres in twenty-four hours. These yields must be taken to apply to the month of January.

On January 3rd we collected twenty-three quart bottles of the gas from the gasometer, which had previously bubbled through potassium hydroxide to deprive it of carbon dioxide, and for a complete analysis one quart bottle. The gas was collected over the water in the King's Well, and each bottle was corked below the water, and packed mouth downwards in a wine case.

The gas was withdrawn from the single bottle into a Töpler's pump, passing through phosphoric oxide so as to dry it. Carbon dioxide was then absorbed from a given volume by means of solid slightly moist potassium hydroxide, melted inside a tube, which was then filled with mercury by means of an inverted siphon. The residual gas introduced into a tube of mercury into which a pellet of phosphorus had been melted, underwent no change of volume; it contained no oxygen.

The composition was: CO_2, 36·0 c.c.; N_2, 964·0 c.c. per litre.

Nearly half a litre (432 c.c.) of this gas was liquefied in a bulb immersed in liquid air, so as to condense carbon dioxide and nitrogen. The gas was originally contained in a mercury gas-holder, connected by pressure-tubing with a reservoir of mercury. By raising the reservoir there was sufficient pressure to condense the gas. The reservoir was lowered somewhat, and a certain amount of the liquid became gaseous. This portion should contain helium and neon, hydrogen and methane, together with nitrogen boiled off. The gasified portion was again condensed, and the operation repeated six times until only 3·406 c.c. remained; 1·881 c.c. of pure oxygen were then added, and sparks were passed. On re-measuring the gas, no change of volume had occurred, nor was any absorption caused by potassium hydroxide. It was therefore impossible to detect hydrogen or methane in half a litre of the gas; this implies at most the absence of 0·01 c.c. of these gases; hence there is not 1 volume of hydrogen or methane in 430,000 volumes of the Bath gas.

The gas from the remaining twenty-three quart bottles, deprived of carbon dioxide, measured 15,916 c.c. at 0°. It was deprived of nitrogen by passing it through red-hot tubes charged with magnesium-lime. The product, consisting of inactive gases, measured 168·3 c.c., corrected for pressure and temperature, or in a litre, 9·894 c.c. This gas was condensed in charcoal cooled with liquid air, as far as was possible; a considerable quantity remained uncondensed; the pressure was then lowered, and a good deal of the gas was removed to a mercury gas-holder. This process was repeated again and again, after the method of fractionation. The final result was three quantities of gas, showing no nitrogen spectrum. The first portion measured 96·6 c.c.; the second, 61 c.c.; and the third, 5·6 c.c.

1*st Portion*.—The weight of a litre of this gas, as a mean of two concordant determinations, was 1·7096 gram; that of a litre of argon is 1·7816, and of neon, 0·9024 gram. The gas contained no helium, nor were the yellow and green lines, which form an exceedingly delicate test for the presence of krypton, to be seen. Calculation shows that this sample of 96·6 c.c. contained 88·7 c.c. of argon and 7·9 c.c. of neon. Its spectrum was in the main that of argon, but neon lines were visible.

2*nd Portion*.—The weight of a litre was 1·3509 gram; the 61 c.c. contained 31·1 c.c. of argon, and 29·9 c.c. of neon. Helium lines were not present in the spectrum, which was mainly that of neon.

3*rd Portion*.—This gas was uncondensable by charcoal; one litre weighed 0·2681 gram. As a litre of helium weighs 0·1777 gram, this density corresponds with a mixture in the 5·6 c.c. of 4·9 c.c. of helium and 0·7 c.c. of neon.

Adding these together, we have in 1 litre of the nitrogen:

Argon, 7·525 c.c.; neon, 2·418 c.c.; and helium, 0·308 c.c.

Reckoned on the total gas, which contains 36 c.c. of carbon dioxide per litre, these numbers become: Argon, 7·263 c.c.; neon, 2·334 c.c.; and helium, 0·297 c.c. Air contains these gases in the proportion:

Argon, 9·32; neon, 0·0124; helium, 0·00408 c.c. per litre.

It is thus evident that the Bath gas contains 0·779 times as much argon, 188·1 times as much neon, and 72·8 times as much helium as are contained in atmospheric air.

In the 5363 litres escaping daily at Bath, there are 39 litres of argon, 12·5 litres of neon, and 1·6 litres of helium. The great preponderance of neon in this gas is discussed in the preceding paper (p. 1367).

Among the gases which escape is niton, or radium emanation. Its measurement by ordinary chemical methods, if not impossible, would be exceedingly difficult, but it can be estimated with great accuracy by its power of ionising the air in an electroscope.

Separate determinations were made for each well. It is possible to express the quantity of niton in four ways: first, as a volume, as is customary for any ordinary gas; secondly, as a weight of radium with which the niton is in equilibrium; thirdly, in "curies," a fraction of 0·6 cubic millimetre, the volume of the niton in equilibrium with 1 gram of metallic radium; and fourthly, in "Mache units," which rest on a purely electrical basis. The first and second methods of expression are most reasonable; the third may be discarded on the ground that, if accepted, we ought then to measure the quantity of oxygen in "Priestleys" or "Scheeles," and that of nitrogen and hydrogen in "Rutherfords" and "Cavendishes"; the fourth method has little chemical significance, and is difficult to interpret.

The weight of 22·380 c.c. of niton at 0° and 760 mm. is 222·35 grams; this is now practically certain. The quantities of niton in natural gases are, however, very small, and are best expressed in fractions of a c.c.

In order to measure the niton, the rate of discharge of an electroscope filled with the Bath gas was compared with the effect produced by the niton which had accumulated during a definite interval of time from a standard solution of radium bromide containing 1/40,000 of a milligram of metallic radium.

The gas from the King's Spring contained $20·2 \times 10^{-12}$ c.c.; or the niton in a million litres of the gas is in equilibrium with 33·65 milligrams of metallic radium.

Gases Dissolved in the Water of the King's Well.—A bottle was filled with the water from the pump-room, pumped up from the King's Well; 285 c.c. of this water were boiled out in a vacuum, and the gas was analysed. It consisted of:

Carbon dioxide..............	6·893 c.c.	per litre of water
Oxygen	1·092 ,,	,, ,,
Nitrogen and inert gases..	13·750 ,,	,, ,,

Analysis of the Residue obtained on Evaporating the Water.

Besides the examination made in the "Lancet" laboratory in 1899, an analysis made by Captain Mackay Heriot in 1874, and quoted in Spender's "The Bath Thermal Waters," is available. To facilitate comparison with our own results, both of these are here expressed in parts per million and in milligrams of ions per litre. A few words as to the methods employed may be prefixed.

The total carbon dioxide was estimated by boiling a known volume of the water with acid. The calcium, iron, etc., were precipitated as oxalate in presence of ammonia from 4·5 litres of the original water; the filtrate was used for magnesium, alkalis, and sulphate; the precipitate, containing hydroxides and oxalates of the remaining metals, was redissolved in hydrochloric acid, and mixed with alcohol to precipitate any sulphates of calcium and strontium present. The small precipitate so obtained was fused with sodium carbonate, converted into nitrate, and treated in the usual way with alcohol and ether to extract strontium. To the main solution, containing calcium, iron, etc., ammonium chloride and ammonium oxalate were added in weakly acid solution; by this means calcium was separated from iron and aluminium, and was weighed as sulphate, together with that from the strontium extraction. Iron and aluminium were next precipitated and weighed together as oxides; their relative amounts were determined in a separate sample of water by extracting their mixed hydroxides with sodium hydroxide prepared from sodium. It was also proved that rare earths were absent, and that there was a small trace of arsenic. The solution containing oxalates, chlorides, and sulphates of the alkali metals and magnesium was evaporated. A small quantity of calcium oxalate which had been in solution was recovered and weighed; the remaining liquid contained magnesium sulphate and alkalis. The magnesium and alkalis were estimated by known methods, and from the chlorides of the alkalis lithium chloride was extracted with amyl alcohol and weighed, and the potassium was estimated as platinichloride.

alysis of the Solid Residue.

	Milligrams per litre.		
	M. & R.	*Lancet.*	Heriot.
Li	0·16	0·28	trace
Na	181·1	159·4	129·0
K	16·7	1·2	39·5
Mg	4·1	57·5	47·4
Ca	335·7	481·6	377·0
Sr	3·2	13·9	trace
Fe	40·2	11·0	6·1
Al	9·7	—	—
As	trace	—	—
Cl	154·8	247·7	280·0
Br	4·4	trace	—
SO_4	1054·0	1278·3	869·0
CO_3	15·8	86·7	86·0
SiO_3	—	24·0	38·0
	1811·0	2362·0	1860·0

	Milligram-equivalents per litre.		
	M. & R.	*Lancet.*	Heriot.
Li	0·02	0·04	trace
Na	7·88	6·93	5·60
K	0·43	0·03	1·01
$\frac{1}{2}$Mg	0·34	4·73	3·88
$\frac{1}{2}$Ca	16·75	24·04	18·76
$\frac{1}{2}$Sr	0·07	0·32	trace
$\frac{1}{2}$Fe	1·44	0·39	0·22
$\frac{1}{3}$Al	1·07	—	—
Cl	4·37	6·98	7·88
Br	0·05	trace	—
$\frac{1}{2}SO_4$	21·74	26·61	18·06
$\frac{1}{2}CO_3$	0·53	2·89	2·86
$\frac{1}{2}SiO_3$	—	0·63	0·78
Metals	27·59	36·48	29·47
Non-metals	26·69	37·11	29·58

Assuming the accuracy of these analyses, it is evident that the composition of the water undergoes considerable fluctuation; this appears also to be the case from Williamson's analyses of the gases. We have been informed that occasionally the water comes up charged with sand, which again disappears after some time.

The water produces a deposit which, as Professor Strutt has shown, contains radium; and radium in the form of a salt is also detectable in the water itself. In order to make this determination, a gallon of the water of the King's Well was boiled for some time, so as to expel all niton; it was then allowed to remain from January 5th until February 13th, so that the full equilibrium quantity of niton should accumulate; the discharging power was then measured against a standard.

The radium as metal amounts to 0·1387 milligram in a million litres of the water; the small quantity is doubtless due to the high percentage of sulphates.

A sample of deposit on the Roman lead pipes, kindly placed at our disposal by Mr. Hatton, consisted mainly of calcium sulphate. It appeared of interest to determine the proportion of radium in it, which would be approximately half of that present in Roman times, for in 1760 years radium has half changed into niton and its products. Ten grams were fused with mixed carbonates in a new crucible, and the carbonates were washed with water until all soluble sulphates were removed; they were then dissolved in dilute hydrochloric acid, and boiled out. In one hundred and forty-three hours the rate of discharge due to niton expelled by boiling was compared with that of the standard; the amount of radium present per gram was $0·97 \times 10^{-7}$ milligram, or about 1 part in 10,000 million by weight. In the modern deposit, consisting mainly of ferric hydroxide and carbonate, radium was not detectable.

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CXLVI.—*The Constitution of the Aldol Bases.*

By Muriel Gwendolen Edwards, Ralph Eddowes Garrod, and Humphrey Owen Jones.

The isomeric compounds, called for brevity "aldol bases," $C_{12}H_{17}ON$, obtained by von Miller and Plöchl (*Ber.*, 1896, **29**, 1462) by the interaction of *m*-4-xylidine and acetaldehyde in dilute hydrochloric acid solution, were given the structural formula

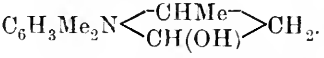
$$C_6H_3Me_2\cdot NH\cdot CHMe\cdot CH_2\cdot CHO,$$

and the isomerism was attributed to a different spatial arrangement of the three groups attached to the tervalent nitrogen atom.

This case of isomerism was studied by one of us and E. J. White (Trans., 1910, **97**, 633), and it was shown that the explanation suggested by von Miller and Plöchl was untenable. The isomerides are not interconvertible under the influence of heat or of organic solvents as stated by these authors, but each is transformed into a mixture of the two by the action of acids. The α-compound (m. p. 103—104°) and the β-compound (m. p. 127—128°) gave the same monobenzoyl derivative by the Schotten-Baumann method, the same derivative with hydroxylamine hydrochloride, and the same condensation product, $C_{20}H_{26}N_2$, bimolecular ethylidenexylidene, or double Schiff's base, with *m*-4-xylidine. The hydrochlorides of the α- and β-bases were, however, different, and so, apparently, were the products obtained by the action of nitrous acid on the bases, but only the derivative of the β-base was obtained crystalline and analysed.

The absorption spectra of the bases was almost identical (Purvis, Trans., 1910, **97**, 644).

It was then suggested tentatively that the bases were structurally different, and might be represented by the formulæ:

$C_6H_3Me_2\cdot NH\cdot CHMe\cdot CH_2\cdot CHO$ and 

$$C_6H_3Me_2N{<}\begin{matrix}CHMe-\\CH(OH)\end{matrix}{>}CH_2.$$

The hydroxytrimethyleneimine ring in the latter compound would probably be unstable (compare Howard and Marckwald, *Ber.*, 1899, **32**, 2031), especially in the presence of acids, and so the formation of a number of identical derivatives would be explained.

The alternative of representing the bases as *cis*- and *trans*-forms of a hydroxytetrahydroquinoline derivative was considered and rejected, mainly because it was considered improbable that the tetrahydroquinoline ring would be so readily formed and would so easily undergo fission.

In the same paper it was shown that two similar isomeric compounds could be obtained from *p*-toluidine and from ψ-cumidine.

The study of these compounds has now been considerably extended, and a thorough examination of the two *p*-toluidine aldol bases has been made; the one isomeride obtainable from 3-bromo-*p*-toluidine, and the more easily obtainable of the two ψ-cumidine aldol bases have also been examined. In all these cases the problem is rendered more difficult owing to the ease with which the aldol bases are converted into a quinoline and a tetrahydroquinoline derivative under the influence of acids or of heat.

The double Schiff's bases, corresponding with bimolecular ethylidenexylidine, from the above amines have also been prepared and their derivatives studied.

Although mesidine and 5-bromo-*m*-4-xylidine have been treated with acetaldehyde under various conditions, no aldol base or double Schiff's base has been obtained from either of these compounds.

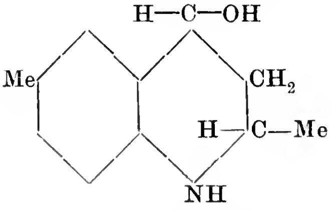
The only fact that seemed inconsistent with the view previously suggested to account for the isomerism of the aldol bases was the apparent existence of two different nitroso-derivatives of the isomeric compounds obtained from *m*-4-xylidine. The whole problem was altered and the clue to its solution obtained when it was clearly established that the two isomeric aldol bases obtained from *p*-toluidine gave two different monobenzoyl derivatives, both insoluble in acids, whereas, as stated above, the α- and β-aldol bases from *m*-4-xylidine had furnished the same derivative.

It was then found that the products of the action of nitrous acid on the α- and β-aldol bases of *m*-4-xylidine could be obtained crystalline, that both were true nitroso-derivatives, $C_{12}H_{16}ON{\cdot}NO$, and that each could be benzoylated and acetylated. The isomeric *p*-toluidine aldol bases also gave nitroso-compounds, which could be benzoylated and acetylated to give isomeric acyl-nitroso-compounds.

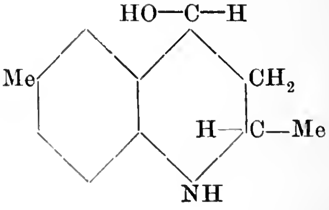
The original α- and β-aldol bases from these acyl nitroso-compounds, when treated with sodium and alcohol, were regenerated. These observations show that each of the isomeric aldol bases is probably a secondary base containing a hydroxyl group.

This conclusion was supported by the fact that the α- and β-xylidine aldol bases gave a dibenzoyl derivative when allowed to remain with benzoyl chloride in pyridine solution from twenty-four to forty-eight hours, and, further, the β-isomeride in the case of *p*-toluidine and xylidine gave a crystalline diacetyl derivative. It is curious, however, that no dibenzoyl compound could be obtained from either of the *p*-toluidine aldol bases.

A consideration of these facts leads to the conclusion that these isomeric bases must be represented as stereoisomeric (*cis* and *trans*) forms of hydroxytetrahydroquinoline derivatives; thus:



and



in the case of the *p*-toluidine compounds.

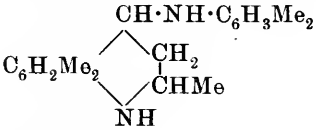
This view accounts for all the facts which we have observed, the most important of which are summarised above, and also for the great similarity which these compounds show in their absorption spectra and physical properties, such as refractive power and viscosity of solutions, which have also been examined and will be described later. On this view, too, the formation of aldol bases from mesidine and 5-bromo-*m*-4-xylidine is impossible.

The hydroxytetrahydroquinoline ring must be very unstable and capable of fission with great ease, especially under the influence of acids, so that the α- and β-bases give the same oxime.

It has been shown that the monobenzoyl derivative (m. p. 150—151°) obtained from both the xylidine aldol bases is really a derivative of the β-aldol base, because on treatment with benzoyl chloride in pyridine solution it is converted into the dibenzoyl derivative of the β-aldol base. It would therefore appear that the α-aldol base or its benzoyl derivative is transformed into the β-compound under the influence of benzoyl chloride or acid in the Schotten-Baumann method of benzoylation.

No compound of the type of these hydroxytetrahydroquinoline derivatives is known, and hitherto we have not been able to reduce the corresponding hydroxyquinoline derivative, 4-hydroxy-2 : 6-dimethylquinoline, and 4-hydroxy-2 : 6 : 8-trimethylquinoline (Conrad and Limpach, *Ber.*, 1888, **21**, 525) to the corresponding hydroxytetrahydroquinoline; alkaline reducing agents have no action on these compounds, whilst acid reducing agents, if they produced the hydroxytetrahydroquinoline, would naturally cause this to undergo transformation into quinoline and tetrahydroquinoline. We have been able to show that tin and hydrochloric acid convert the above hydroxyquinoline derivatives into the corresponding tetrahydroquinoline derivatives, a change which is best explained by the intermediate formation of a hydroxytetrahydroquinoline or aldol base.

The double Schiff's bases, $C_{20}H_{26}N_2$ in the case of xylidine, might be constituted similarly to the aldol bases, that is:



or they might be represented as

$$C_6H_3Me_2\cdot NH\cdot CHMe\cdot CH_2\cdot CH{:}N\cdot C_6H_3Me_2,$$

as suggested by von Miller and Plöchl.

A study of their properties supports the second mode of representation, as they give monoacetyl, monobenzoyl, and mononitroso-derivatives only, but it follows that the tetrahydroquinoline ring must be broken by mere heating with xylidine in the case of the α- and β-xylidine aldol bases, which are thus converted into the double Schiff's base. This change does not take place in the case of the *p*-toluidine aldol bases.

EXPERIMENTAL.

p-*Toluidine Derivatives. α- and β-Aldol Bases,* $C_{11}H_{15}ON$.

A mixture of the isomeric bases was prepared by the action of acetaldehyde on *p*-toluidine (Trans., 1910, **97**, 643) in a manner analogous to that used in the case of the corresponding xylidine compounds. In this case, however, a small quantity of a brown, tarry material was always produced, and was difficult to remove entirely from the α-compound.

The separation of the α- and β-isomerides was effected by shaking the mixture with alcohol (40 grams of mixture to 200 c.c. of alcohol), when the β-base melting at 164—167° (when heated rapidly, 165—169°) was obtained practically pure from the undissolved solid, and was recrystallised from alcohol, from which it separated in lustrous plates.

The α-base was isolated by evaporation of the alcoholic solution. The coloured product was purified by repeated recrystallisation from benzene or petroleum (b. p. 90—100°), and separated in soft, brittle plates, melting at 108—110°.

The wide range of melting in the case of these two bases is due to the fact that, even at the lower temperature, the quinoline transformation has already set in, and is rapid at the melting point of the β-base.

Either isomeride, when treated with sodium and alcohol, was recovered unchanged.

Derivatives of p-*Toluidine Aldol Bases.*

Action of Hydrogen Chloride.—On passing dry hydrogen chloride into a solution of the β-base in ether or benzene, the hydrochloride separated as a white powder, melting at 126—127°.

Under similar conditions, the α-hydrochloride separated as a white powder, but was extremely deliquescent, and when left exposed to the air for some hours, at first became viscid, and then appeared to become dry, when it was found to have been converted into the β-hydrochloride.

Oxime.—By the action of hydroxylamine hydrochloride in alcohol and water, the same oxime was obtained from both α- and β-aldol base, the yield being very poor. The substance was recrystallised from alcohol, and melted at 132—134°:

0·1372 gave 0·3459 CO_2 and 0·1061 H_2O. C=68·7; H=8·6.

$C_{11}H_{16}ON_2$ requires C=68·8; H=8·34 per cent.

Acyl Derivatives of p-*Toluidine Aldol Bases.*

Action of Acetyl Chloride.

β-Compound.—Acetylation was conducted in pyridine solution, the product separating from rectified spirit in very well defined, short, lustrous prisms or diamond-shaped plates, melting at 117—119°, which were only sparingly soluble in light petroleum:

0·1965 gave 0·4930 CO_2 and 0·1275 H_2O. C=68·6; H=7·2.
0·1235 „ 5·7 c.c. N_2 at 14° and 754 mm. N=5·5.
$C_{15}H_{19}O_3N$ requires C=69·0; H=7·28; N=5·36 per cent.

The compound is therefore a diacetyl derivative.

The *α-derivative,* similarly prepared, was a gum, and could not be obtained crystalline.

Benzoyl Compounds.—The benzoyl derivatives of the α- and β-bases were prepared by the Schotten-Baumann process, and were recrystallised from benzene. The *β-compound* was obtained in short prisms or stout, rectangular plates, tending to form stellate aggregates, and melting at 170—172°:

0·2143 gave 0·5985 CO_2 and 0·1322 H_2O. C=76·3; H=6·85.
$C_{18}H_{19}O_2N$ requires C=76·8; H=6·76 per cent.

The *α-compound* separated from benzene in long needles, melting at 145—146°, which tended to be quite thin and to form a felted mass:

0·2081 gave 9·3 c.c. N_2 at 17° and 722 mm. N=5·03.
$C_{18}H_{19}O_2N$ requires N=4·98 per cent.

This is therefore a monobenzoyl derivative.

Both α- and β-aldol bases gave the same monobenzoyl derivatives in pyridine solution as by the Schotten-Baumann process, in striking contrast to the corresponding xylidine compounds.

Action of Nitrous Acid.

*β-*p-*Toluidine Aldol Base.*—1·77 Grams of the base dissolved in 30 c.c. of *N*-sulphuric acid were cooled and quickly poured into a solution of 2·5 grams of sodium nitrite in 300 c.c. of cold water. An oil separated, which crystallised on keeping, and was purified by crystallisation from alcohol, or, better, from benzene, when it formed long, yellow prisms, melting at 108—110°:

0·2015 gave 0·4710 CO_2 and 0·1290 H_2O. C=63·8; H=7·11.
$C_{11}H_{14}O_2N_2$ requires C=64·1; H=6·8 per cent.

The same product was obtained when one molecular proportion of sodium nitrite, dissolved in water, was poured into the aldol base solution. In the case of the α-toluidine aldol base, either method only gave a viscid substance, which did not crystallise. The pure β-compound and the oil obtained from the α-base gave Liebermann's nitroso-reaction, and were insoluble in acids. They would therefore appear to be nitroso-compounds of secondary amines, and on reduction the original aldol bases were recovered.

Benzoylation of Nitroso-derivatives.

The nitroso-compounds obtained from the α- and β-aldol bases were benzoylated by the Schotten-Baumann method.

Benzoyl-nitroso-β-aldol Base.—The compound separated from benzene in yellow plates mixed with a few needles, melting at 124—125°, and having a duller brown tinge than the original nitroso-derivative:

0·2023 gave 0·5180 CO_2 and 0·1062 H_2O. C=69·8; H=5·8.

$C_{18}H_{18}O_3N_2$ requires C=69·7; H=5·81; N=9·04 per cent.

The compound was therefore a benzoyl-nitroso-derivative. It gave Liebermann's nitroso-reaction. On reduction with sodium and alcohol, ammonia was evolved, and the β-*p*-toluidine aldol base obtained, so that removal of the nitroso- and benzoyl groups occurred simultaneously.

Benzoyl-nitroso-α-aldol Base.—The compound which was prepared from the viscid α-nitroso-compound separated from alcohol in yellow needles, melting at 130—132°, and brighter in colour than the corresponding β-compound. When mixed with the latter, the mixture melted at 107—110°:

0·2024 gave 0·5147 CO_2 and 0·1070 H_2O. C=69·4; H=5·8.

0·2825 ,, 23·2 c.c. N_2 at 19° and 740 mm. N=9·4.

This is therefore a benzoyl-nitroso-compound isomeric with that obtained from the β-aldol base, and, like it, giving Liebermann's test.

On reduction with sodium and alcohol, ammonia was evolved, and the α-*p*-toluidine aldol base obtained, contaminated with a trace of the β-base, that is, in this case also the nitroso- and benzoyl groups were removed simultaneously. No change was produced by the action of the aluminium-mercury couple and alcoholic sodium hydroxide, or by hydrogen and colloidal palladium.

Action of Acetyl Chloride on the Nitroso-compounds.

The nitroso-compounds of the α- and β-*p*-toluidine aldol bases do not give such well-characterised acetyl compounds as the corresponding xylidine derivatives when treated with acetyl chloride in pyridine solution, but the β-compound was obtained crystalline in yellow prisms, which were somewhat difficult to recrystallise, and tended to become viscid, so that they could not be obtained pure. They melted at 68—69°:

0·2691 gave 26·0 c.c. N_2 at 16° and 751 mm. N = 11·3.

$C_{13}H_{16}O_3N_2$ requires N = 11·3 per cent.

Double Schiff's Base of p-*Toluidine.*

This compound was prepared by neutralising a mixture of toluidine and acetaldehyde in equimolecular proportions in hydrochloric acid after allowing it to remain for one to two hours. The product was sparingly soluble in light petroleum, and soluble in alcohol, thereby differing from the corresponding xylidine compound. It separates from alcohol in well-defined, lustrous prisms, melting at 114—116°:

0·2010 gave 0·5970 CO_2 and 0·1495 H_2O. C = 81·0; H = 8·27.

0·3918 „ 35·2 c.c. N_2 at 13° and 753 mm. N = 10·7.

$C_{18}H_{22}N_2$ requires C = 81·2; H = 8·27; N = 10·5 per cent.

From its method of production and the fact that none can be obtained after the reaction mixture has remained for several hours, it would appear that the formation of this compound precedes the formation of the isomeric aldol base.

The acetyl compound formed in pyridine solution could not be obtained crystalline.

The *nitroso*-derivative was produced by pouring a solution of the base in dilute sulphuric acid into excess of dilute sodium nitrite in the cold. The yellow precipitate was collected and dissolved in alcohol, from which it separated in brownish-yellow plates, melting at 135·7:

0·2135 gave 26·0 c.c. N_2 at 15° and 764 mm. N = 14·6.

$C_{18}H_{21}ON_3$ requires N = 14·2 per cent.

The compound is therefore a mononitroso-derivative.

m-4-*Xylidine Aldol Bases and Derivatives.*

The preparation and separation of these isomeric bases has been already described (Trans., 1910, **97**, 635), together with that of the derived oxime, benzoyl compound, and products of the action of hydrogen chloride.

A preliminary mechanical separation was generally necessary in the preparation of the α- and β-aldol bases, although occasionally by fractional crystallisation a crop of practically pure crystals of α-compound (m. p. 103—104°) was obtained. The less soluble β-compound melting at 127—128° is quite easily obtained in a state of purity.

Acetyl Derivatives of m-4-*Xylidine Aldol Bases.*

Acetylation of the β-aldol base was effected in pyridine, the product being difficult to crystallise. It separated from ether, and very well from petroleum, in rectangular prisms and hexagonal plates melting at 94—95°:

0·2200 gave 0·5625 CO_2 and 0·1505 H_2O. C=69·7; H=7·6.
0·3575 „ 16·4 c.c. N_2 at 18° and 754 mm. N=5·38.
$C_{16}H_{21}O_3N$ requires C=69·8; H=7·64; N=5·1 per cent.

The derivative was therefore a diacetyl compound. The acetyl derivative of the α-aldol base was obtained as a gum, which crystallised, only after long keeping, in thin plates melting at 70—71°.

Benzoyl Compounds of α- and β-Xylidine Aldol Bases.

By the Schotten-Baumann method the same monobenzoyl compound, melting at 150—151°, is obtained from both isomerides as previously mentioned (Jones and White, Trans., 1910, **97**, 641). In order to see if the same result was obtained under different conditions, the mixture of the α- or β-aldol base with benzoyl chloride in pyridine solution was allowed to remain for twenty-four or forty-eight hours.

α-Xylidine-aldol base thus gave a product which separated from alcohol in well-defined, lustrous prisms, melting at 143—144°. A mixture of this with the monobenzoyl compound melted at 122—126°:

0·1935 gave 0·5550 CO_2 and 0·1075 H_2O. C=78·2; H=6·17.
0·3190 „ 10·0 c.c. N_2 at 21° and 743 mm. N=3·56.
$C_{26}H_{25}O_3N$ requires C=78·2; H=6·27; N=3·51 per cent.

The compound is therefore a dibenzoyl derivative of the α-aldol base, in which both the secondary nitrogen and the hydroxyl group have reacted with benzoyl chloride.

β-Xylidine aldol base, when treated in the same way, gave a product which separated from alcohol in flat prisms and plates melting at 145—146°.

A mixture of this with the monobenzoyl compound melted at 128—134°, and a mixture with the compound obtained from the α-base melted below 125°:

0·4847 gave 15·0 c.c. N_2 at 19° and 739 mm. N=3·53.

The compound is therefore a dibenzoyl derivative different from the dibenzoyl derivative of the α-base.

On treating the monobenzoyl derivative (m. p. 150—151°) with benzoyl chloride in pyridine solution, a compound identical with the dibenzoyl derivative of the β-aldol base was obtained, so that the compound produced by the Schotten-Baumann method is to be regarded as a derivative of the β-aldol base.

Action of Nitrous Acid.—The product from the β-base has been already described (*loc. cit.*, p. 642), and has since been obtained in pale yellow, lustrous octahedra, melting at 117°.

Xylidine α-Aldol Base and Nitrous Acid.

To 1·91 grams of the α-base dissolved in 20 c.c. of *N*-sulphuric acid were added gradually 0·7 gram (1 molecular proportion) of sodium nitrite dissolved in 150 c.c. of water. The oily precipitate which formed was extracted with benzene, from which solvent long, slender, yellow prisms separated, melting at 80—81°:

0·1485 gave 0·3575 CO_2 and 0·0970 H_2O. C=65·6; H=7·26.
0·1759 „ 18·7 c.c. N_2 at 18° and 741 mm. N=12·3.
$C_{12}H_{16}O_2N_2$ requires C=65·5; H=7·27; N=12·7 per cent.

so that the compound is a mononitroso-derivative.

The reduction of either the α- or β-nitroso-compound with sodium and alcohol regenerated the corresponding aldol base.

When 0·6 gram of the α-aldol base dissolved in 10 c.c. of *N*-sulphuric acid was poured into a solution of 0·8 gram of sodium nitrite dissolved in 50 c.c. of cold water, and extracted with petroleum, a yellow, crystalline solid separated, melting at 92—98°, but this could not be recrystallised. On repeating the process with larger quantities, prisms separated, melting at 97—103°. A mixture of these with the β-nitroso-derivative melted at 80°.

Analyses were made of three different specimens after drying in a vacuum, and very concordant results were obtained, of which one may be quoted as typical:

0·2380 gave 0·5030 CO_2 and 0·1345 H_2O. C=57·7; H=6·3.
0·1867 „ 26·45 c.c. N_2 at 18° and 766 mm. N=16·8.
$C_{12}H_{16}O_3N_3$ requires C=57·6; H=6·4; N=16·8 per cent.

and it was therefore concluded that this compound was an additive compound of the NO-group and a nitroso-derivative, or possibly it is a dinitroso-compound. No evidence is available for deciding the position of the second nitroso-group.

Action of Benzoyl Chloride on Nitroso-β-xylidine Aldol Base.

As the Schotten-Baumann method tried in two experiments was not satisfactory, the action of benzoyl chloride in pyridine was investigated.

To 1·91 grams of the nitroso-compound dissolved in 20 c.c. of pyridine were added 1·4 grams of benzoyl chloride, and the whole was allowed to remain for four hours, after which it was poured into dilute sulphuric acid and extracted with ether. The product separated from rectified spirit in almost colourless, rectangular prisms, melting at 110—111°, and giving a well-marked Liebermann reaction:

0·2018 gave 0·5205 CO_2 and 0·1140 H_2O. C=70·3; H=6·28.

$C_{19}H_{20}O_3N_2$ requires C=70·3; H=6·17 per cent.

The compound is therefore a benzoyl-nitroso-derivative.

On heating the above substance a gas is evolved, slowly at 160° and rapidly at 170°.

Benzoyl chloride appeared to have no action on the nitroso-derivative of the *α*-aldol base in presence of sodium hydroxide or in pyridine solution after a few hours. On allowing the mixture in pyridine to remain for two days a viscid oil was obtained, which only showed signs of crystallising after keeping for a long time.

Action of Acetyl Chloride on Nitroso-β-xylidine Aldol Base.

The product obtained in pyridine separated from alcohol in pale yellow, rectangular prisms, melting at 110—111°, giving Liebermann's reaction, and remaining unchanged when boiled with sodium hydroxide solution:

0·2357 gave 0·5560 CO_2 and 0·1500 H_2O. C=64·3; H=7·07.
0·3012 „ 28·1 c.c. N_2 at 15° and 735·5 mm. N=10·7.

$C_{14}H_{18}O_3N_2$ requires C=64·1; H=6·87; N=10·7 per cent.

Acetyl-nitroso-derivative of the α-Aldol Base.

In pyridine a gum was obtained which crystallised on keeping, and separated from alcohol in pale yellow, rectangular prisms, melting at 87—89°:

0·2865 gave 27·1 c.c. N_2 at 17° and 755·5 mm. N=11·0.

$C_{14}H_{18}O_3N_2$ requires N=10·7 per cent.

The nitroso-derivatives of the *α*- and *β*-aldol bases therefore react with acetyl chloride to yield different acetyl-nitroso-compounds.

Derivatives of Double Schiff's Base of m-4-*Xylidine.*

The *hydrochloride* was precipitated in colourless needles by passing dry hydrogen chloride into a solution of the base in light petroleum. On keeping, it became coloured, and was found to change into a mixture of xylidine with quinoline derivatives:

0·2030 gave 0·1566 AgCl. Cl=19·1.

$C_{20}H_{26}N_2,2HCl$ requires Cl=19·3 per cent.

The *compound* with trinitrobenzene separated from alcohol in black, lustrous prisms, melting at 132°:

0·2752 gave 0·5380 CO_2 and 0·1115 H_2O. C=53·3; H=4·50.
$C_{20}H_{26}N_2,2C_6H_3O_6N_3$ requires C=53·3; H=4·44 per cent.

The *acetyl* derivative was prepared in pyridine solution, and separated from alcohol in fine rhombs melting at 144—145°:

0·1920 gave 0·5515 CO_2 and 0·1434 H_2O. C=78·4; H=8·30.
$C_{22}H_{28}ON_2$ requires C=78·6; H=8·33 per cent.

The compound is therefore a monoacetyl derivative.

The *benzoyl* derivative obtained by the Schotten-Baumann method separated from alcohol in lustrous needles melting at 192—193°:

0·3330 gave 19·6 c.c. N_2 at 17° and 752 mm. N=6·91.
$C_{27}H_{30}ON_2$ requires N=7·0 per cent.

The double Schiff's base therefore gives a monoacetyl and a monobenzoyl derivative.

The action of nitrous acid under various conditions gave a pale yellow, granular precipitate, insoluble in water, but readily soluble in organic solvents, from which it separated as a gum. Analysis of this gave results which were intermediate between the values calculated for mono- and di-nitroso-compounds.

3-*Bromo*-p-*toluidine Aldol Base.*

This substance was prepared by mixing 15·5 grams of 3-bromo-*p*-toluidine with 450 c.c. of 5 per cent. hydrochloric acid, after which about 500 c.c. of water were introduced to clear the solution of precipitated hydrochloride. Eleven c.c. of acetaldehyde were then poured in slowly with shaking. After eighteen hours a slight precipitate was usually formed and 5·5 c.c. more aldehyde were added, the mixture being allowed to remain for four hours more. It was then filtered through glass-wool, 80 c.c. of light petroleum added, and the liquid neutralised by potassium hydroxide with vigorous shaking.

The aldol base separated between the two layers, and after an hour was collected, washed with light petroleum, and crystallised from alcohol, from which it separated in needles melting at 144—145°. The substance was practically pure, and no trace of an isomeride could be discovered:

0·1605 gave 0·3030 CO_2 and 0·0745 H_2O. C=51·5; H=5·6.
$C_{11}H_{14}ONBr$ requires C=51·6; H=5·47 per cent.

The base is unaffected either by sodium and alcohol or by the aluminium-mercury couple and sodium hydroxide solution.

The *hydrochloride* obtained by precipitation from ether melted at 123°, and from it the base could be recovered unchanged.

There is no reaction with benzoyl chloride by the Schotten-Baumann method, nor yet in pyridine solution.

The *acetyl* derivative of the bromo-*p*-toluidine aldol base is formed in pyridine solution, and separates from alcohol in diamond-shaped plates melting at 83—85°:

0·1505 gave 0·2880 CO_2 and 0·0771 H_2O. C=52·2; H=5·66.
0·3023 „ 12·0 c.c. N_2 at 17° and 752 mm. N=4·67.
$C_{13}H_{16}O_2NBr$ requires C=52·3; H=5·37; N=4·7 per cent.

The compound is therefore a monoacetyl derivative.

*The Nitroso-derivative of Bromo-*p*-toluidine Aldol Base.*

This substance separated from alcohol in small, yellow needles, melting at 136—137°:

0·2045 gave 0·3440 CO_2 and 0·0855 H_2O. C=45·9; H=4·65.
$C_{11}H_{13}O_2N_2Br$ requires C=46·3; H=4·57 per cent.

The *acetylnitroso*-compound of the bromo-*p*-toluidine aldol base separates from alcohol in small, yellow plates, melting at 136—137°:

0·1792 gave 13·7 c.c. at 14° and 748 mm. N=8·78.
$C_{13}H_{15}O_3N_2Br$ requires N=8·57 per cent.

*Double Schiff's Base of Bromo-*p*-toluidine.*

The precipitate which separated from the reaction mixture on keeping was found to be the double Schiff's base, but it was better prepared as described below.

To 15·5 grams of bromo-*p*-toluidine dissolved in 500 c.c. of alcohol, 5·5 c.c. of acetaldehyde were added. After two days, no change having occurred, a few drops of concentrated hydrochloric acid were added. After one day a crystalline precipitate melting at 135—138° appeared. After recrystallisation from petroleum it melted at 144—146°, and the mixture with the aldol base of bromo-*p*-toluidine melted at 126—130°:

0·1882 gave 0·3490 CO_2 and 0·0798 H_2O. C=50·6; H=4·7.
$(C_9H_{10}NBr)_2$ requires C=50·9; H=4·72 per cent.

Therefore, although a diacetyl compound is not formed, the aldol base is capable of reacting as if it contained both an NH- and an OH-group.

ψ-Cumidine Aldol Base.

From the product of the action of acetaldehyde on ψ-cumidine in hydrochloric acid only one of the two isomeric aldol bases which are formed (Trans., 1910, **97**, 643) could be isolated pure in sufficient quantity with which to work. This, the β aldol base, was crystallised from benzene and light petroleum, from which it separated in colourless needles melting at 110—112°.

The Benzoyl Derivative of the β-ψ-Cumidine Aldol Base.

The aldol base was treated with benzoyl chloride in pyridine solution, and yielded a substance which crystallises from alcohol in fine needles melting at 240—241°:

0·3228 gave 12·7 c.c. N_2 at 16° and 745 mm. N = 4·59.

$C_{20}H_{23}O_2N$ requires N = 4·53 per cent.

The compound is therefore a monobenzoyl derivative.

Acetyl chloride in pyridine solution seems to have little or no action on the aldol base, as the reaction mixture was completely soluble in acid.

The *nitroso*-compound of the β-ψ-cumidine aldol base was prepared in the usual way and crystallised from ether, when it separated in stumpy prisms and plates melting at 110—112°:

0·2667 gave 26·8 c.c. N_2 at 19° and 759 mm. N = 11·8.

$C_{13}H_{18}O_2N_2$ requires N = 12·0 per cent.

The compound is therefore a mononitroso-derivative.

The expenses of this work have been partly defrayed by grants from the Government Grant Committee of the Royal Society and from the University of Wales, for which we are glad to make this grateful acknowledgment.

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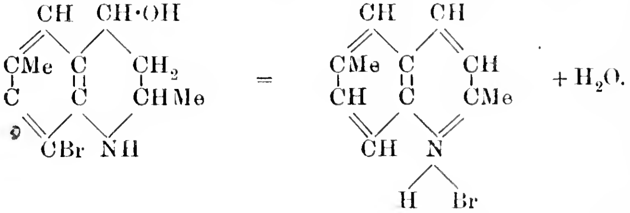
CXLVII.—*Some Quinoline and Tetrahydroquinoline Derivatives obtained from Aldol Bases.*

By RALPH EDDOWES GARROD, HUMPHREY OWEN JONES, and PERCY EDWIN EVANS.

IN the course of the study of the constitution and properties of the aldol bases (this vol., p. 1376) and of their conversion under the influence of heat or of acids into quinoline and tetrahydroquinoline derivatives, which will be described at a future date, the behaviour of the aldol bases prepared from 3-bromo-*p*-toluidine and from ψ-cumidine has been examined.

The behaviour of the aldol base derived from 3-bromo-*p*-toluidine is interesting and peculiar. This paper contains a brief account of this and of some new quinoline and tetrahydroquinoline derivatives prepared from 3-bromo-*p*-toluidine and from *ψ*-cumidine, and also of some derivatives of the compounds obtained from *m*-4-xylidine which have been prepared in the course of this and other work which is in progress.

The aldol base of 3-bromo-*p*-toluidine when heated alone to about 180—200° is converted quantitatively into the hydrobromide of 2:6-dimethylquinoline according to the following scheme:



When the same base is treated with acids, either in the cold or at 100°, the main product is 8-bromo-2:6-dimethylquinoline, formed according to the scheme:

$$C_{11}H_{14}ONBr = C_{11}H_{10}NBr + H_2O + H_2.$$

In this case the hydrogen which is eliminated from one molecule is not quite completely used up in reducing another molecule of quinoline to the corresponding tetrahydro-derivative, but a small proportion of it attacks the bromoquinoline, removing the bromine as hydrogen bromide, and producing 2:6-dimethylquinoline.

The reaction which takes place on heating the aldol base of *ψ*-cumidine is exactly similar to that which was observed in the case of the *m*-4-xylidine compounds (Trans., 1911, **99**, 334), and may be represented by the equation:

$$2C_{13}H_{19}ON = C_{13}H_{15}N + C_{13}H_{19}N + 2H_2O.$$

The 2:5:6:8-tetramethylquinoline and 2:5:6:8-tetramethyltetrahydroquinoline which are produced in equimolecular proportions were separated by means of the benzoyl compound or the nitroso-compound of the latter.

*Action of Heat and of Acids on the Aldol Base of 3-Bromo-*p*-toluidine.*

The preparation and properties of the aldol base are described in the preceding paper (this vol., p. 1387). The yield is poor, as much of the double Schiff's base is formed; this may, however, be used for the preparation of 8-bromo-2:6-dimethylquinoline.

On heating the aldol base to 150—170° even for several days no change seems to occur, and the unchanged base may be recovered; at about 180—200°, however, in the course of a few hours the liquid solidified to a solid soluble in water, which was identified as the hydrobromide of 2:6-dimethylquinoline. 0·5795 Gram, on heating to 210° for two hours, left 0·5334 gram of solid, from which 0·4178 gram of silver bromide was obtained, that is, 98 per cent. of the bromine was recovered as silver bromide.

The change which takes place on heating the aldol base is therefore represented by the equation given above.

On boiling the aldol base of 3-bromo-*p*-toluidine with mineral acid (for example, 10 per cent. hydrochloric acid or 20 per cent. sulphuric acid) for several hours and neutralising the liquid, a crystalline solid was deposited. This solid contained some secondary base, which was removed by treatment with benzoyl chloride or with nitrous acid.

The tertiary base was recovered from the acid solution and recrystallised from benzene or light petroleum, from which it separated in colourless, square plates containing bromine, and melting at 96—97°:

0·2022 gave 0·4117 CO_2 and 0·0768 H_2O. $C=55·5$; $H=4·22$.

$C_{11}H_{10}NBr$ requires $C=55·9$; $H=4·24$ per cent.

This compound is therefore 8-*bromo*-2:6-*dimethylquinoline.*

The *hydrochloride* separates from aqueous solutions in needles melting at 150—151°:

0·3011 gave 0·1565 AgCl. $Cl=12·9$.

$C_{11}H_{10}NBr,HCl$ requires $Cl=13·0$ per cent.

The *platinichloride* forms yellow needles, sparingly soluble in water, and melting and decomposing at 211—212°:

0·7010 gave 0·1515 Pt. $Pt=21·6$.

$(C_{11}H_{10}NBr)_2,H_2PtCl_6$ requires $Pt=22·1$ per cent.

The *picrate* separates from alcohol, in which it is sparingly soluble, in yellow needles melting at 158—159°:

0·2020 gave 21 c.c. N_2 at 16° and 751 mm. $N=12·3$.

$C_{17}H_{13}O_7N_4Br$ requires $N=12·1$ per cent.

The two atoms of hydrogen which are eliminated from the molecule of the aldol base do not, in this as in the cases of the other aldol bases examined, react quantitatively to produce a tetrahydroquinoline derivative, as the acid solution after boiling always contained some hydrobromic acid. Two experiments were made to determine the amount of this:

0·8215 gram of aldol base was boiled with dilute sulphuric acid for five hours, after which the solution gave 0·0323 gram of silver bromide, which corresponds with 5·4 per cent. of the total bromine present.

1·7910 grams boiled for nine hours gave 0·0638 gram of silver bromide, corresponding with 4·87 per cent. of total bromine.

Some of the hydrogen therefore reduces the bromodimethylquinoline with removal of bromine, but this is comparatively only a small quantity; the rest reduces 8-bromo-2:6-dimethylquinoline to 8-bromo-2:6-dimethyltetrahydroquinoline, the benzoyl derivative of which was obtained from the mixture. This separates from alcohol in bright, lustrous rhombs, melting at 143—144°:

0·2040 gave 0·4681 CO_2 and 0·0961 H_2O. C = 62·6; H = 5·23.
0·3262 ,, 12·4 c.c. N_2 at 17° and 754 mm. N = 4·3.
$C_{18}H_{18}ONBr$ requires C = 62·8; H = 5·23; N = 4·07 per cent.

This compound is therefore 8-*bromo*-1-*benzoyl*-2:6-*dimethyltetrahydroquinoline.*

Attempts to prepare bromodimethyltetrahydroquinoline by the action of tin and hydrochloric acid on bromodimethylquinoline simply resulted in the production of 2:6-dimethyltetrahydroquinoline, the bromine being removed during the reduction.

Preparation of 2:5:6:8-*Tetramethylquinoline and* 2:5:6:8-*Tetramethyltetrahydroquinoline from the ψ-Cumidine Aldol Bases.*

The mixed aldol bases were prepared from ψ-cumidine by mixing 11 grams of base dissolved in 120 c.c. of hydrochloric acid solution (containing 6 grams of HCl) with 11 c.c. of acetaldehyde, keeping for about eighteen hours, and then neutralising in presence of 40 c.c. of light petroleum. The aldol bases, which soon separated as a white, crystalline cake, were collected and dried.

On heating to about 160° for five or six hours the aldol bases are completely transformed into an oil, which distilled between 289° and 292°/764 mm. In this way 33·5 grams of ψ-cumidine yielded 33 grams of mixed aldol bases, and on heating and distilling, 30·5 grams of mixed quinoline and tetrahydroquinoline derivatives were obtained.

This mixture was separated by benzoylation, the benzoyl compound was repeatedly washed with acid, dried, and then weighed 22 grams. The tertiary base dissolved in the acid was liberated, collected, and weighed 14·8 grams. It was recognised as 2:5:6:8-tetramethylquinoline (*Ber.*, 1886, **17**, 1710). This compound is described as an oil, but the specimen prepared as described above solidified, on keeping, to lustrous plates melting at 28°. (Found, C = 84·0; H = 8·15. $C_{13}H_{15}N$ requires C = 84·3; H = 8·11 per cent.)

The above observations show that the reaction proceeds quantitatively according to the equation given above, and in the same manner as the reaction studied in the case of the xylidine aldol bases (*loc. cit.*).

The following compounds of 2:5:6:8-tetramethylquinoline were also prepared:

The *hydrochloride* separates from aqueous solution in colourless needles melting at 244°.

The *picrate* crystallises from hot alcohol in stellate aggregates of needles, and melts at 179°.

The *platinichloride* is a buff, microcrystalline powder, melting and decomposing at 248°.

Benzoyl-2:5:6:8-*tetramethyltetrahydroquinoline* was recrystallised from hot alcohol, and separated in fine needles melting at 254°:

0·2070 gave 0·6202 CO_2 and 0·1435 H_2O. C = 81·7; H = 7·7.
$C_{20}H_{23}ON$ requires C = 81 9; H = 7·85 per cent.

On boiling with concentrated hydrochloric acid for a long time the benzoyl compound gradually dissolved, and the base was recovered from the solution.

On boiling the mixed aldol bases from ψ-cumidine with mineral acids for several hours, the same change was found to take place. The cooled solution was treated with dilute sodium nitrite solution, the oily nitroso-compound of 2:5:6:8-tetramethyltetrahydroquinoline was removed by ether, and 2:5:6:8-tetramethylquinoline recovered from the solution.

The nitroso-compound was reconverted into the base by treatment with tin and hydrochloric acid.

2:5:6:8-*Tetramethyltetrahydroquinoline* was obtained as an oil boiling at 290—292°/756 mm.

The *hydrochloride* separates from aqueous solution in colourless needles, melting and decomposing at 252°:

0·4890 gave 0·3065 AgCl. Cl = 15·5.
$C_{13}H_{19}N,HCl$ requires Cl = 15·7 per cent.

The *picrate* separates from hot alcohol, in which it is sparingly soluble, in small, pale yellow needles, melting at 181—182°:

0·1757 gave 20·2 c.c. N_2 at 17° and 766 mm. N = 13·5.
$C_{13}H_{19}N,C_6H_3O_7N_3$ requires N = 13·4 per cent.

The *platinichloride* separates as a buff, microcrystalline powder, which decomposes on heating.

Some new derivatives of 2:6:8-trimethylquinoline and 2:6:8-trimethyltetrahydroquinoline have also been prepared in the course of the study of the changes by which these are formed from the α- and β-*m*-4-xylidine aldol bases.

The *trinitrobenzene compound* of 2:6:8-*trimethylquinoline* separates from alcoholic solution in brown needles melting at 121—123°:

0·2170 gave 0·4440 CO_2 and 0·0830 H_2O. C=55·8; H=4·2.

$C_{12}H_{13}N,C_6H_3O_6N_3$ requires C=56·3; H=4·16 per cent.

The *trinitrobenzene compound* of 2:6:8-*trimethyltetrahydroquinoline* separates from alcohol in black needles melting at 95—96°:

0·2092 gave 0·4270 CO_2 and 0·0945 H_2O. C=55·7; H=5·02.

$C_{12}H_{17}N,C_6H_3O_6N_3$ requires C=55·7; H=5·15 per cent.

The *periodide* of 2:6:8-*trimethylquinoline* separates from a solution of the base in hydrochloric acid on addition of a solution of iodine in potassium iodide as dark brown needles, which are very sparingly soluble in water and melt at 151—152°:

0·3240 gave 0·3080 CO_2 and 0·0740 H_2O. C=25·9; H=2·5.

$C_{12}H_{13}N,HI,I_2$ requires C=26·0; H=2·53 per cent.

The corresponding *periodide* of 2:6:8-*trimethyltetrahydroquinoline* also separates in dark brown needles under the same conditions when recrystallised from alcohol; these melted at 155—156°.

1-*Nitroso*-2:6:8-*trimethyltetrahydroquinoline* is precipitated in crystalline form on the addition of dilute sodium nitrite solution to a solution of the base in dilute acid.

It separates from alcohol in pale yellow needles melting at 68—69°:

0·2120 gave 0·5475 CO_2 and 0·1435 H_2O. C=70·4; H=7·52.

$C_{12}H_{16}ON_2$ requires C=70·6; H=7·88 per cent.

The expenses of this work have been largely defrayed by grants from the Government Grant Committee of the Royal Society, for which we are glad to make this grateful acknowledgment.

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CXLVIII.—*Blue Adsorption Compounds of Iodine. Part I. Starch, Saponarin, and Cholalic Acid.*

By GEORGE BARGER and ELLEN FIELD.

THE so-called "iodide" of starch has been the subject of much investigation, and not a little controversy. Many stoicheiometric formulæ have been proposed for it, with iodine content varying from 3 to 20 per cent. This is not surprising, since starch is not a chemical individual, and since the blue substance loses iodine so readily that it cannot be isolated, and must be analysed by indirect methods.

The multiplicity of formulæ which have been suggested is in itself an argument against the correctness of any one of them, and Küster (*Annalen*, 1894, **283**, 360) has shown that the iodine content of the "starch iodide" changes continuously with the concentration of the iodine solution with which it is in equilibrium; moreover, the ratio of partition between starch and water is not constant either, but varies between wide limits. Küster, rejecting the formulæ of Mylius (*Ber.*, 1887, **20**, 688) and of other investigators, considered that the blue substance is a solid solution of iodine in starch. In any case, if starch and iodine form a stoicheiometrical compound at all, such compound is readily dissociated, and for this reason several chemists have of late employed physico-chemical methods; thus Friedenthal (*Centr. Physiol.*, 1899, **13**, 54) used the depression of the freezing point; Rodewald and Kattein (*Zeitsch. physikal. Chem.*, 1900, **33**, 586) measured the osmotic pressure of starch iodide. Andrews and Goettsch (*J. Amer. Chem. Soc.*, 1902, **24**, 865) measured the vapour pressure of iodine in starch solutions, and the partition-coefficient of iodine between starch solutions and chloroform. Padoa and Savarè (*Gazzetta*, 1906, **36**, i, 313) have employed electrical conductivity, and Katayama (*Zeitsch. anorg. Chem.*, 1907, **56**, 209) used a tintometric method.* Harrison (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 5) considers that in the case of starch an adsorption compound is formed similar to the purple of Cassius, and attempted to prepare colloidal blue iodine solutions.

The blue compound of iodine and starch is by no means without analogues. A number of other substances behave to iodine in a similar manner. Of these, cholalic acid and basic lanthanum acetate have been examined more closely, the former by Mylius (*Ber.*, 1887, **20**, 683) and by Küster (*Zeitsch. physikal. Chem.*, 1895, **16**, 156), the latter by Biltz (*Ber.*, 1904, **37**, 719).

The present investigation was undertaken in the hope that further insight into this phenomenon might be obtained by a comparative study of as many examples as are available, and particularly by the application of recent advances in the chemistry of colloids. In the case of starch iodide the connexion with colloids is obvious, but has apparently only been taken into account by Padoa and Savarè and to some extent by Katayama, and particularly by Harrison. Biltz bases his interpretation of the behaviour of iodine to basic lanthanum acetate on the colloidal nature of the latter

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* A bibliography of the literature on starch "iodide" up to 1902 is given by Andrews and Goettsch in their paper referred to above.

substance, which he considers to be coloured blue by adsorption of the iodine.

So far as we can see at present, the substances under discussion may be roughly classified in three groups, according to their dispersivity:

I. The first group comprises highly colloidal substances, such as starch, basic lanthanum acetate, the product of the action of 70 per cent. sulphuric acid on cellulose, thallonic acid, *iso*lichinin, and various other ill-defined plant substances. In this group the blue compound is never obtained other than amorphous.

II. The members of this group are crystalline semi-colloids, with a molecular weight of something like 500; the blue compound is generally obtainable, both in the amorphous and in the crystalline condition. Examples are: cholalic acid and the glucoside saponarin, with which this paper is more particularly concerned.

III. In the third group the blue iodine compound is only known in the crystalline state, as in the case of the alkaloid narceine. Another example of this class is the product of the action of iodine on ergoxantheine, recently recognised as such by one of us, in conjunction with A. J. Ewins (Trans., 1911, **99**, 2338, footnote). Possibly the second and third of these groups are not sharply differentiated.

The Blue Substance from Saponarin: its Colloidal Properties.

In this section we propose to show that iodine, under certain conditions, changes saponarin to a well-marked suspension colloid. Comparison will also be made with starch iodide, where the lyophobic properties are much less marked.

Saponarin is a glucoside, occurring dissolved in the cell sap of a number of plants; on addition of iodine in potassium iodide the whole of the cell contents is coloured blue, so that the substance was regarded by botanists as a naturally occurring "soluble starch." It was first isolated from *Saponaria officinalis* by one of us (Trans., 1906, **89**, 1210), and was identified as the glucoside of the colouring matter vitexin, first obtained by A. G. Perkin (Trans., 1898, **73**, 1030; 1900, **77**, 416). The formula of saponarin is $C_{21}H_{24}O_{12} = 468$, and the glucoside is readily obtained pure in minute needles by crystallisation from water and pyridine. It has a slight ("true") solubility in water; by shaking, filtering, and evaporating, 1 part was found to dissolve in 7100 parts of water at 18°. The aqueous solution, so obtained, is not coloured blue by iodine, nor are the crystals themselves coloured when shaken with iodine solution. In this respect saponarin differs from starch, for solid starch is coloured under these conditions, and starch has no true solubility in water. The aqueous solution of saponarin, formed by shaking in the cold, is molecular disperse, and such solutions are apparently never coloured blue. For the production of the blue compound a colloidal solution, or the formation of the solid in the presence of iodine, are necessary.

Colloidal solutions of saponarin are obtained by dissolving the glucoside in alkali, in pyridine, or in formamide, and acidifying or diluting with water. Less concentrated hydrosols, free from other substances, may also be obtained by boiling the glucoside with water, when about 1 gram per litre dissolves. (It is best to use a quartz vessel, so as to exclude the alkali of glass.) The solutions obtained in any of these ways do not deposit the glucoside at laboratory temperature for some days, but finally saponarin crystallises out. These "supersaturated" solutions are colloidal.

Under the ultra-microscope they can be resolved, an observation made possible by the kindness of Dr. W. M. Bayliss, F.R.S. Such a solution also shows the Tyndall effect, but is not opalescent to the naked eye.

Colloidal solutions of saponarin are coloured blue by iodine in potassium iodide*; on diluting the blue hydrosol with water a point is reached at which the blue colour vanishes more or less abruptly. At this dilution evidently the true solubility has been reached, and the whole of the saponarin is molecular-disperse. In accordance with this, we find that the blue colour persists at a dilution of 1:7000, but has disappeared at 1:9000. The solubility at 18° is 1:7100.

There is nothing analogous to this in starch solutions, because the dispersivity is never sufficiently great; on this fact the use of starch as an indicator depends.

When a little iodine in potassium iodide solution is added to a saponarin solution free from electrolytes (obtained by boiling with water), a blue hydrosol results, which under the ordinary microscope is homogeneous, and passes through filter paper or porous clay; the addition of electrolytes causes the separation of blue flakes. Concentrated hydrosols, prepared by acidification of an alkaline solution, set to a thick jelly on the addition of iodine, so that a test-tube containing it may be inverted without loss.

The precipitant effect of different ions was investigated as follows: 0·080 gram of crystalline saponarin, $C_{21}H_{24}O_{12},2H_2O$, was dissolved in about 80 c.c. of water, by boiling in a quartz flask, and after cooling was made up to 100 c.c. Then 25 c.c. of $N/100$-iodine in potassium iodide solution were added (1·27 grams of iodine and

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* In the cell sap of *Saponaria* the glucoside is probably held in solution by saponins.

2·5 grams of potassium iodide per litre). Of the resulting blue solution quantities of 5 c.c. were run into test-tubes, and to each was added 1 c.c. of various electrolyte solutions; the final concentration of the glucoside was therefore 0·00107 mol. per litre. The minimum concentration of the electrolyte was determined, which resolved the blue hydrosol into distinct flakes within one minute. The final concentrations required to do this were as follows, expressed in millimols. per litre:

Saponarin, 1·07 *Millimols. per Litre.*

	Millimols.		Millimols.
KCl	51	$\frac{Al_2(SO_4)_3}{2}$	0·21
KNO_3	49	$AlCl_3$	0·22
KI	60	$Co(NH_3)_6Cl_3$	0·1
$\frac{K_2SO_4}{2}$	53	$Th(NO_3)_4$	0·2
$\frac{\text{K tartrate}}{2}$	50	HCl	58
$NaCl$	53	HNO_3	66
NH_4Cl	53	$\frac{H_2SO_4}{2}$	78
$LiCl$	75	$CCl_3{\cdot}CO_2H$	88
Aniline hydrochloride	50	$CHCl_2{\cdot}CO_2H$	195
Morphine ,,	no action	$\frac{H_3PO_4}{3}$	482
$BaCl_2$	1·8	$CH_2Cl{\cdot}CO_2H$	no action
$SrCl_2$	2·25	$CH_3{\cdot}CO_2H$	,,
$CaCl_2$	2·6	$C_2H_2O_4$	,,
$La(NO_3)_3$	0·2		

It should be noted that the saponarin–iodine solution employed in all these experiments itself contained already potassium iodide equivalent to a final concentration of about 2·5 millimols., but part of this is not in aqueous solution, as will be shown later, and since an increase in KI concentration of 60 millimols. was required to produce flocculation, the error due to the potassium iodide originally present is at most a few per cent.

From a consideration of the above table it is evident that the saponarin–iodine compound behaves like a typical negative lyophobic (or suspension) colloid; the average concentrations of uni-, bi-, and ter-valent cations required to produce precipitation are approximately in the ratio 50 : 2·2 : 0·2, and afford a good illustration of Schulze's law.

The negative colloidal nature of the substance is also evident in cataphoresis. The blue solution used in the flocculation experiments, placed in a **U**-tube with platinum electrodes, moves towards the anode.

This is similar to starch iodide, which also moves to the anode, as was already found by Padoa and Savarè. According to recent experiments of Bottazzi and Victoroff (*Atti R. Accad. Lincei,* 1910, [v], **19**, ii, 7), pure amylose is electrically neutral.

We were unable to investigate the cataphoretic behaviour of saponarin itself, because the solution does not show a boundary surface against distilled water; perhaps this might be done ultra-microscopically. In any case, however, a colloidal solution of saponarin differs entirely from that of its "iodide" in not being precipitated by electrolytes; saponarin itself is lyophilic, and only becomes lyophobic by addition of iodine. The case is therefore opposite to that of a gold solution protected by gelatin.

As in the case of gold, we may imagine that the surface tension between gold and water is decreased by the formation of a gelatin film on the gold particle; so we consider that the surface tension between the two phases of the saponarin solution is diminished by the deposit on the colloidal particles of a film of iodine, or of an iodine compound. This would mean that iodine is adsorbed by the saponarin particles, for which other evidence will be adduced later.

Cases of this kind are rare; Michaelis and Rona (*Biochem. Zeitsch.*, 1907, **21**, 11) have based a method for the removal of protein from solution on the fact that with mastic the protein can be made to yield an adsorption compound which is precipitated by small quantities of electrolytes. The mastic here corresponds with the iodine, and the protein to the saponarin. If iodine were obtainable in colloidal solution it would, no doubt, behave like a suspension colloid. We have tried to prepare colloidal solutions of iodine (by the interaction of hydriodic and iodic acids), but without success. In this connexion it should be noted that many brown solutions of iodine in organic solvents are resolvable under the ultra-microscope (Amann, *Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 235).

The blue substance formed from saponarin is thus characterised as a negative colloid by its cataphoretic behaviour and by its susceptibility to cations. It was therefore to be expected that it would be precipitated by colloids of opposite sign, and we find that it is flocculated by methylene-blue and by night-blue (both positive), but not by azo-blue (negative). The same saponarin–iodine solution was used as had been employed for investigating the ionic flocculation. Of this solution 5 c.c. required 1 c.c. of 0·08—0·1 per cent. methylene-blue. The precipitate settles down rapidly, and the supernatant fluid is pale yellow. With larger quantities of methylene-blue the whole of the saponarin iodide is still precipitated, but this is not so with the highly colloidal night-blue, which shows a well-marked optimal flocculation zone. Again, 1 c.c. of the dye solution was added to 5 c.c. of the solution of the saponarin iodide; 0·1 per cent. night-blue gave no flocculation, 0·12 per cent. slight, and 0·5 per cent. complete precipitation of the saponarin, but with 2 per cent. night-blue the flocculation was again very slight.

These results are similar to those of Teague and Buxton (*Zeitsch. physikal. Chem.*, 1907, **60**, 469) on the mutual flocculation of oppositely charged dyes. The saponarin iodide behaves like a moderately colloidal negative dye, which is completely precipitated by methylene-blue at all concentrations above a certain value, but by highly colloidal dyes like night-blue only when their concentration is between certain limits, so that in the latter case there is both a supra-optimal and an infra-optimal zone.

The blue hydrosol of saponarin and iodine is not precipitated by electronegative dyes, such as azo-blue, at any concentration.

Behaviour of Starch Iodide to Electrolytes and to Dyes.

As was said above, starch iodide wanders to the anode; it should therefore behave to salts and other colloids in the same way as the corresponding saponarin compound.

Qualitatively this was found to be the case, although quantitatively there are considerable differences on account of the highly colloidal nature of starch; the adsorption of iodine does not so completely abolish its lyophilic properties.

Five c.c. of a 1 per cent. solution of soluble starch was mixed with 5 c.c. of $N/10$-iodine in potassium iodide and 5 c.c. of a salt solution. The final concentration of the salt required to produce immediate flocculation was 180 millimols. for potassium chloride and 30 millimols. for barium chloride. The amount of iodine added was large, so as to ensure considerable adsorption; small quantities of iodine are insufficient to render the starch lyophobic, and even with large quantities of iodine the blue substance is much less readily precipitated than in the case of saponarin.

The blue starch solution was completely flocculated by methylene-blue at all final concentrations of the dye in excess of 0·07 per cent.; azo-blue did not flocculate at all. With night-blue there is a well-marked optimal zone, even with much less iodine.

4 c.c. 1 per cent. starch; 1 c.c. $N/100$-iodine; 1 c.c. night-blue.

1 c.c. night-blue	0·4 per cent.	slight floculation
1 c.c. ,,	0·5 ,,	greater ,,
1 c.c. ,,	0·8 ,,	complete ,,
1 c.c. ,,	1·0 ,,	no ,,
1 c.c. ,,	2·0 ,,	no ,,

In this respect also there is therefore a fairly close analogy between the blue compounds from starch and from saponarin. The more highly colloidal nature of starch brings about a greater adsorption or "affinity" for iodine; thus the saponarin compound is much more readily decolorised by warming, and by the addition of organic solvents of iodine. The blue saponarin compound can also be obtained in the form of blue needles by allowing a solution of the glucoside in dilute acetic acid, to which iodine in potassium iodide has been added, to evaporate at the ordinary temperature on a watch-glass. In this respect saponarin resembles cholalic acid, to be discussed later.

Composition of the Blue Substance from Saponarin.

The composition of the hydrosol can only be studied by physical methods, and for this purpose Padoa and Savarè used electrical conductivity in the case of starch.

We find that the conductance of a saponarin solution and a solution of iodine in potassium iodide is less after mixing than before, proving that some of the potassium iodide has become adsorbed; but we have not yet carried out a systematic investigation of this point. For the estimation of the "free" iodine, the solutions were prepared by mixing measured volumes of standard iodine solutions with measured volumes of 0·1 per cent. saponarin solution and flocculation by addition of half the volume of 10 per cent. sulphuric acid, as in Küster's experiments. In these the starch iodide settled down, so that, on keeping, enough of the clear, supernatant liquid could be withdrawn by means of a pipette, but with saponarin no such separation takes place, so that it was necessary to filter. Paper is objectionable as it takes up a considerable quantity of iodine, and the same objection was found to apply also to asbestos, but not to glass-wool. By packing the latter fairly loosely in a glass funnel, the blue flakes could be collected, so that the iodine in the filtrate could be determined by titration with $N/100$-thiosulphate (and starch). In the calculation, by difference, of the amount of iodine in the blue gel, the volume of the latter was neglected. In the following table are given the concentrations of free iodine remaining in solution and taken up by the saponarin, expressed both in grams and gram-atoms.

In the fifth column the value has been calculated according to Freundlich's formula, $x/m = ac^{1/n}$; the values of a and $1/n$ were obtained graphically.

$$a = 1\cdot23 ;\ 1/n = 0\cdot167.$$

Grams of iodine per litre of filtrate	Grams of iodine per gram of saponarin.	c = gram atoms of iodine per litre.	$x/m = \frac{\text{atoms of iodine}}{\text{mol. of saponarin}}$	x/m (calc.)
0·0533	0·080	0·00042	0·317	0·337
0·171	0·109	0·00134	0·432	0·409
0·376	0·124	0·00294	0·491	0·466
0·606	0·131	0·00477	0·519	0·505
0·792	0·133	0·00623	0·527	0·528

These results cannot lay claim to great accuracy on account of the small concentration of the saponarin solution obtainable by boiling with water (0·1 per cent.). It is, however, evident from column 4 that the blue precipitate does not correspond with any simple chemical compound over a limited range; its composition may be expressed by an exponential adsorption formula; in concentrated iodine solutions the iodine content of the saponarin reaches a maximum at about 16 per cent. The existence of such a maximum for charcoal has lately been recognised by G. C. Schmidt (*Zeitsch. physikal. Chem.*, 1910, **74**, 689) and by Marc (*ibid.*, 1911, **76**, 58).

As is well known, the blue substances formed from starch and from cholalic acid contain potassium iodide as well as free iodine; the same holds good for saponarin. The adsorption of potassium iodide by a saponarin hydrosol can be shown directly by conductivity determinations, and after flocculation the amount can be determined quantitatively.

A solution of iodine in water free from iodide does not colour starch, or cholalic acid, or saponarin. The addition of potassium iodide in all cases then brings about immediate coloration. It was at first thought that the iodide ion was specific, but in the case of saponarin this is not so. Many electrolytes will bring about the adsorption of the iodine, and although it is impossible to exclude the formation of iodine ions by double decomposition, it is the valency of the cation which appears to be of most importance, as seen from the following.

In each case 2 c.c. of saponarin (0·08 per cent.) (prepared in a quartz vessel) were mixed with 5 c.c. of saturated solution of iodine in water, and 1 c.c. of the following were added:

1 c.c. H_2O in 53′, very pale green tint.
1 ,, $M/100$-$LaCl_3$ in 10′, deep green; in 20′, deep blue and flocculated.
1 ,, $M/100$-$AlCl_3$, no effect.
1 ,, $M/10$-$BaCl_2$ in 20′, deep green; in 30′, blue.
1 ,, M-KCl in 38′, green; later, solution became blue.

The inactivity of aluminium chloride is perhaps due to hydrolytic dissociation. With starch it is difficult to obtain regular results, but in a simple comparative experiment the great activity of lanthanum salts in favouring adsorption, as compared with potassium salts, can be shown. The best example of this phenomenon is euxanthic acid, which, it is hoped, will be dealt with in a future paper. Cholalic acid does not show anything similar. The favourable effect of neutral salts is here analogous to that observed by Bayliss in the adsorption of electronegative colloids by filter paper (*Biochem. J.*, 1906, **1**, 195), and of trypsin by various substances, including soluble starch (*Proc. Roy. Soc.*, 1911, *B*, **84**, 88). Bayliss' explanation, in terms of the present case, would be that electronegative iodine is not adsorbed by electronegative starch or saponarin until the charge on the saponarin has been reversed by the cation of the salt. On this presupposes that colloidal iodine would be electronegative, which is, a priori, probable.

The Red Iodides of Saponarin and of Starch.

A further effect on salts remains to be discussed, which is only evident in concentrated solution. Potassium iodide changes the colour of starch iodide from blue, through purple, to crimson, and the same takes place with saponarin. Mylius (*loc. cit.*) and Hale (*Amer. Chem. J.*, 1902, **28**, 438) both found for the blue iodide the ratio 4I:HI, and for the red substance 2I:HI. On dilution with water the red iodide again became blue; according to Hale the changes may be expressed thus:

$$\underset{\text{Blue.}}{KI{\cdot}I_4 + KI} \rightleftarrows \underset{\text{Red.}}{2KI{\cdot}I_2}$$

Our own experiments with saponarin so far indicate that this change is physical rather than chemical. The blue saponarin iodide when dried becomes red, but immediately becomes blue again on adding water. The change from blue to red is not only brought about by iodides, but also by bromides at greater concentration, and by thiocyanates at much smaller concentration.

This suggests a lyotropic effect of the anion (Freundlich, "Kapillarchemie," 1909, pp. 54 and 418). We used 45 c.c. of 1 per cent. starch and 5 c.c. of *N*/100-iodine in potassium iodide. The crimson iodide was produced with potassium thiocyanate at a final concentration of 0·28 mol., with potassium iodide 0·40 mol.; with potassium bromide, 2·1 mol., there was no effect, but in a saturated solution the blue iodide also becomes crimson. The effects with saponarin were similar, and the blue compound also becomes purple in a saturated ammonium nitrate solution (potassium nitrate is not sufficiently soluble). Ammonium chloride and sulphate were without effect, even in saturated solution. The anions come, therefore, in the same order as that in which they inhibit the setting of gelatin sols, namely:

SCN, I, Br, NO_3, Cl, and SO_4.

Cholalic Acid.

The blue compound of iodine and cholalic acid is remarkable for the ease with which it is obtained crystalline. If iodine in potassium iodide is added to an alcoholic solution of cholalic acid in the right proportion, the compound separates out on dilution with water in deep blue needles. The substance was analysed by Mylius (*Ber.*, 1887, **20**, 683), who gave it the formula $(C_{24}H_{40}O_5I)_4KI$, analogous to the formula $(C_{24}H_{40}O_{20}I)_4KI$, assigned by him to starch iodide.

Küster having disproved the latter formula for starch iodide, investigated the cholalic acid compound (*Zeitsch. physikal. Chem.*, 1895, **16**, 156), and concluded that a crystalline additive compound is formed (Krystallstrukturverbindung) similar to the molecular compounds of cholalic acid with water, alcohols, acetone, etc. This compound can only exist in the solid condition, and is only formed in solutions of a definite minimum iodine concentration.

Since these results differ considerably from those obtained for starch, we repeated Küster's experiments, with very similar results. Four grams of pure cholalic acid, dried at 100°, were dissolved in 100 c.c. of 70 per cent. alcohol. For each determination 10 c.c. of this solution were mixed with a known quantity of *N*/10-iodine in potassium iodide, and diluted with water to 100 c.c. After remaining overnight, the solutions were filtered through glass-wool, and the iodine in 50 c.c. of the filtrate was determined by titration.

	C.c. of *N*/10-iodine added.	C.c. of *N*/10-iodine left in solution.	Gram of iodine in cholalic acid.
1	1·046	0·067	0·0124
2	1 48	0·21	0·0161
3	2·09	0·24	0·0235
4	2·95	0·36	0·0329
5	5·05	0·40	0·0591
6	9·92	2·00	0·0906
7	15·28	6·00	0·1139
8	19·70	10·75	0·1137
9	25·10	15·97	0·1159

The precipitates in the first three or four experiments were at first yellow; No. 2 became green after about ten minutes, and then blue; No. 3 more rapidly; No. 4 almost at once. Under the microscope No. 2 was found to consist of many pale amorphous particles with a few blue needles; in No. 4 there were but few such particles; No. 6 was almost homogeneous, and consisted of blue needles; No. 9

had a metallic lustre, and when 10 c.c. of 4 per cent. cholalic acid were mixed with 90 c.c. of $N/10$-iodine the precipitate was brown, and consisted of brown, amorphous particles with a few pale blue needles.

Like Küster, we find that the blue compound is not formed until the iodine in solution reaches a certain concentration; in Küster's experiments this is recorded as 0·02 gram in 100 c.c., or $N/635$. In our own experiments this limit is not quite constant, but is 0·2—0·4 c.c. of $N/10$-iodine per 100 c.c., that is, $N/5000$—$N/2500$, or 0·0025—0·005 gram per 100 c.c. This difference may be due to the fact that, in order to avoid the adsorption of iodine by filter paper (an error experienced by Küster), we used glass-wool; the result was that in 1--5 the filtrate was turbid, although not blue. Experiments 8 and 9 represent the conditions recommended by Mylius for the production of the blue crystals, and in these cases the solution filtered readily through glass-wool.

In calculating the percentage of iodine in cholalic acid, Küster allowed for nearly 10 per cent. of acid, which passed through the filter "uncombined" with iodine. In our own experiments this quantity as determined by titration with barium hydroxide was only about 0·015 gram in each experiment. It follows that 0·385 gram of cholalic acid dried at 100° and free from alcohol of crystallisation combines in experiments 7—9 with 0·1139, 0·1137, and 0·1159 gram of iodine, that is, 29·5—30·1 per cent. of its own weight. Küster found in corresponding experiments 29·6—31·0 per cent. referred to the acid containing alcohol of crystallisation, and therefore 32·6—34·1 per cent. of the acid free from alcohol. Mylius' formula requires that the alcohol-free acid should take up 31·1 per cent. of free iodine, a value intermediate between Küster's value and that obtained by ourselves. The concentrations of the solutions in the last two experiments of both series correspond with those recommended by Mylius for the preparation of the blue, crystalline iodide, and it would indeed appear as if a dissociable stoicheiometrical compound is formed when the iodine concentration exceeds a certain definite value. This compound crystallises with great readiness; cholalic acid, precipitated from alcoholic solution by water or by potassium iodide solution, was amorphous, and did not become crystalline until after long keeping; thus in the experiments 1—6, where insufficient iodine was used, the whole of the blue compound was crystalline, the rest of the acid amorphous. The case of the crystalline iodide of cholalic acid is thus very different from that of the amorphous, blue substances formed from starch, lanthanum acetate, and saponarin, where adsorption plays a great part. In the case of the blue crystals from cholalic acid, adsorption is apparently not wholly excluded, for their iodine content may slightly exceed that of one atomic proportion.

If cholalic acid, however, separates in the presence of iodine in the amorphous condition, adsorption is greatly increased, and the phenomenon resembles much more closely the effect of iodine in starch, etc. For this purpose we used an aqueous solution of pure sodium cholalate, to which iodine in different amounts was added; on acidification a blue compound separates, which remains amorphous, and may contain much more iodine than the crystalline substance formed in the presence of alcohol. The sodium cholalate employed was crystallised by adding acetone to a concentrated solution of cholalic acid in the theoretical amount of sodium hydroxide. We employed an aqueous solution containing 1·29 per cent. (0·03 mol.) of the dry salt, and in all experiments this was finally diluted, by the addition of iodine solution and of hydrochloric acid, to three times its original volume, so that the final concentration of the cholalic acid was in all cases 0·408 per cent., or 0·01 mol., and therefore much the same as in Küster's and our previous experiments with alcoholic solutions.

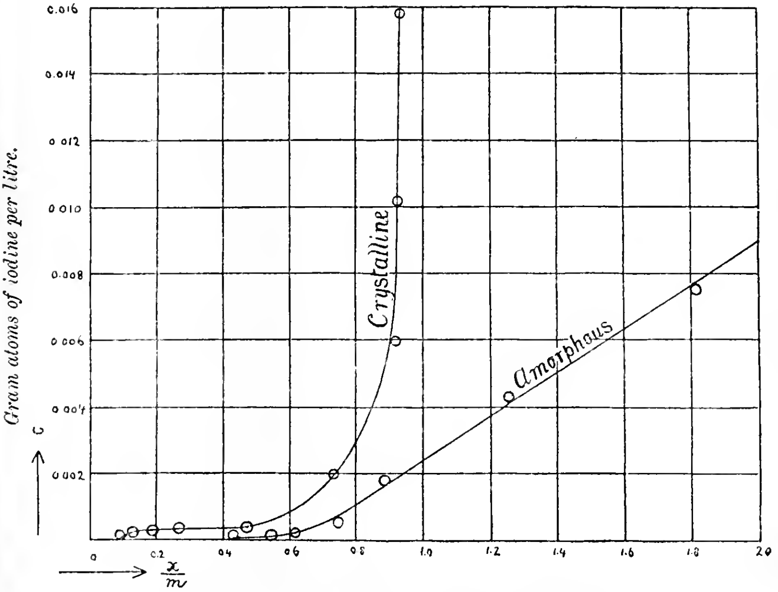
In the following table are given, in column 2, the concentration of iodine in gram-atoms per litre which would have resulted had no iodine been taken up by the cholalic acid; column 3 gives the concentration, *C*, of the filtrate in gram-atoms per litre; column 4 shows the amount of iodine in grams per gram of cholalic acid; in columns 5 and 6 the observed and the calculated values of x/m or gram-atoms of iodine per gram-molecule of cholalic acid are given; the calculation was made according to the formula $x/m = \alpha c^{1/n}$, where

$$\alpha = 2{\cdot}58\,;\ 1/n = 0{\cdot}168.$$

Exp.		*C*.		x/m found.	x/m calc.	
1……	0·0056	0·000099	0·171	0·55	0·55	blue
2……	0·0067	0·000227	0·193	0·62	0·63	,,
3……	0·0083	0·00063	0·243	0·78	0·75	,,
4……	0·0111	0·00185	0·277	0·89	0·89	,,
5……	0·0167	0·00425	0·392	1·26	[1·03]	black
6……	0·0250	0·00766	0·564	1·81	[1·14]	,,
7……	0·0333	0·0130	0·650	2·09	[1·24]	brown

In the last column is given the colour of the resulting precipitate; where this is pure blue the adsorption formula is followed closely over a limited range, but with higher concentrations of iodine the precipitate became steel-grey to black, red in thin layers, and finally brown. This brown substance contains much more iodine, and to some extent resembles certain periodides. On the addition of very little sodium hyposulphite the brown colour is changed to blue. Obviously, then, in experiments 5—7 a further addition of iodine has taken place.

If we compare the composition of the amorphous, blue precipitate formed from the sodium salt with that of the crystals obtained by diluting an alcoholic solution, the extent to which the amorphous state favours adsorption is evident. Both sets of results (from the two preceding tables) are plotted in the accompanying figure, which shows how in the latter case the iodine approximates to one atomic proportion, which is greatly exceeded in the former case.



Gram atoms of iodine per molecule of cholalic acid.

Colloidal Properties of the Iodide of Cholalic Acid.

The blue iodide behaves to cations like a negative colloid. 0·5 Gram cholalic acid was dissolved in 10 c.c. of absolute alcohol, and after the addition of 15 c.c. of $N/10$-iodine in potassium iodide the whole was made up with water to 1 litre. To 5 c.c. of the blue solution 1 c.c. of various salt solutions was added, and the concentrations noted, which flocculated in one minute. The final concentrations of the salts were as follows:

KCl	35 millimols.
$BaCl_2$	0·5 ,,
$AlCl_3$	0·03 ,,
$Co(NH_3)_6Cl_3$	0·016 ,,

As in the case of saponarin the most powerful salt was luteocobaltic chloride, which was tried at the suggestion of Mr. G. R. Mines, who kindly supplied us with a specimen. An alcoholic solution of cholalic acid, without iodine, diluted with water in the same way yields a turbid suspension which has quite different properties, for example, it is not flocculated at a concentration of 166 millimols. of lanthanum nitrate.

The blue iodide further behaves to dyes in the same way as saponarin. A solution similar to that employed with salts, but diluted only to 500 c.c., was used in quantities of 5 c.c., each with 1 c.c. of the dye solution. Methylene-blue (0·05 per cent.) produces no flocculation; 1 c.c. of a 0·1 per cent. solution flocculated completely; 1 c.c. of a 1 per cent. solution also completely. Night-blue showed an optimum zone as with saponarin.

Cholalic acid differs from starch and saponarin in not yielding a crimson compound with iodine at high concentrations of potassium iodide or of potassium thiocyanate.

General Conclusions.

So far we are led to the view that the blue substances under discussion when crystalline may be additive products of iodine in atomic proportion; but whenever they are colloidal and separate in the amorphous state, there is also a considerable adsorption of iodine. This is particularly the case with starch.

The presence of electrolytes (potassium iodide) is necessary to bring about this adsorption by means of the cation.

No substance which is dissolved as separate molecules gives a blue colour with iodine; this is only obtained either with colloids or with other substances when they separate from a solution containing iodine.

The blue substances formed behave as negative suspension colloids which have been rendered lyophobic by the iodine adsorbed.

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CXLIX.—*The Viscosity of Ether–Alcohol Mixtures.*

By Frank Baker.

For many years it has been known that mixtures of alcohols and ethers possess the property of dissolving certain varieties of nitrocellulose, although the latter compounds are insoluble in either component. Of this fact advantage is taken in the preparation of collodion and in the manufacture of a number of smokeless powders.

At first sight it might appear that this property of ether–alcohol mixtures is fully analogous to the power possessed by other alcoholic solutions of gelatinising or dissolving nitrocellulose; thus, in the manufacture of celluloid a methyl or ethyl alcoholic solution of camphor is used as a gelatinising agent, whilst solutions in alcohol of a large number of other compounds, such as various nitro-compounds, esters, acetylated aromatic amines, etc., have been proposed for the same purpose.

The latter type of solvent differs from the ether–alcohol class in that the non-alcohol component is one which contains some grouping known to be favourable to gelatinising power—the ketonic group in camphor, for example—and the employment of alcohol is due only to the practical difficulties which would be encountered in using the substances in the pure state. From these considerations it would appear that some chemical change takes place when alcohols and ethers are mixed.

The study of the viscosity of liquid mixtures has, within recent years, added much to our knowledge of these mixtures. Whilst this work has shown conclusively that even in the case of mixtures of non-associated liquids the viscosity of mixtures cannot be calculated by any simple law (Lees, *Phil. Mag.*, 1901, [vi], **1**, 128), certain relationships have been found between the curves obtained when the viscosities are plotted against the proportions of the components (Dunstan, Trans., 1907, **91**, 83).

In cases where reaction is known to take place when liquids are mixed, abnormal curves are obtained. Mixtures of alcohols and water, for example, generally give curves showing well-marked maxima, ascribed to association (Dunstan, Trans., 1909, **95**, 1556); in other cases maxima due apparently to dissociation have been observed (Dunstan, Trans., 1904, **85**, 817).

Consideration of the above made it appear highly probable that viscosity determinations of mixtures of alcohols and ethers would give some clue to the cause of the solvent properties of such mixtures, and with this object the following work was undertaken.

EXPERIMENTAL.

For the determination of the viscosity of the liquids examined, viscometers of the Ostwald type were used. Two instruments were employed of the following dimensions:

Capacity of upper bulb	= 7 c.c.	8 c.c.
Radius of capillary	= 0·2 mm.	0·2 mm.
Length of capillary	= 180 ,,	180 ,,
Mean difference of level	= 190 ,,	100 ,,

During the experiments, the viscometer was immersed in a thermostat of about 40 litres capacity with glass windows. The temperature of this bath was controlled by a toluene regulator, and the variations of temperature did not exceed ±0·02°. The thermometer was compared with an instrument standardised at the National Physical Laboratory.

The determinations of the density of the liquids were carried out in a Sprengel tube of 25 c.c. capacity. The probable error of these determinations, as shown by the agreement between duplicate results, was about one part in 10,000.

The times of flow were determined with an accuracy of 0·2″ with a tested stop-watch. In nearly all cases duplicate tests agreed within 0·4″, and as the times of flow were never less than 400″ these readings had an accuracy of at least 0·1 per cent. The mixtures were made up by weight, 40 c.c. of the mixture being used, and the weights determined to 1 milligram.

From the above it would appear that the error in determining the viscosities of the mixtures employed was less than 0·1 per cent. This, of course, would be true only if the relation $\frac{d_1t_1}{d_2t_2} = \frac{\eta_1}{\eta_2}$ were correct for the viscometers employed to this degree of accuracy.

For this relation to hold, the Hagenbach correction and also the error due to differences in surface tension must be small. As regards the first source of error, the viscometers used had approximately the same dimensions as those employed by Appleby (Trans., 1910, **97**, 2000), for which this correction was shown to be negligible.

The latter source of error would appear, according to the last-named, to be somewhat considerable. An attempt was, however, made to minimise it by using viscometers with bulbs of nearly the same dimensions. As, in addition, except in standardising the viscometers, liquids of considerably lower surface tensions than water were used, no allowance was regarded as necessary for this source of error.

The methyl alcohol, ethyl alcohol, and ethyl ether were bought to very stringent specifications, and were redistilled through a Young's column before use. The remaining substances were obtained from Kahlbaum's, and were carefully redistilled before use. In each case the boiling point was found to be constant.

Mixtures of the following liquids were studied:

Methyl alcohol with ethyl ether, anisole, and phenetole; ethyl alcohol with ethyl ether, anisole, and phenetole, and ethyl ether with propyl and benzyl alcohols.

The results are given in the following tables:

Methyl Alcohol and Ethyl Ether.

Ether. Per cent.	Density.	Viscosity.	Ether. Per cent.	Density.	Viscosity.
0·00	0·7880	0·005506	60·23	0·7457	0·003378
23·12	0·7731	0·004734	73·08	0·7349	0·002953
35·07	0·7648	0·004296	86·33	0·7226	0·002553
47·40	0·7559	0·003846	100·00	0·7075	0·002260

Ethyl Alcohol and Ethyl Ether.

0·00	0·7880	0·01112	72·99	0·7336	0·003152
23·15	0·7724	0·007414	78·37	0·7291	0·002897
47·43	0·7546	0·004782	86·39	0·7218	0·002635
57·51	0·7464	0·004005	100·00	0·7075	0·002260
64·48	0·7408	0·003590	—	—	—

n-*Propyl Alcohol and Ethyl Ether.*

0·00	0·8010	0·01971	47·16	0·7594	0·005619
11·93	0·7918	0·01404	59·89	0·7473	0·004274
22·99	0·7818	0·01024	72·97	0·7341	0·003355
34·92	0·7730	0·007528	86·22	0·7200	0·002717
—	—	—	100·00	0·7075	0 002260

Methyl Alcohol and Anisole.

Anisole. Per cent.	Density.	Viscosity.	Anisole. Per cent.	Density.	Viscosity.
0·00	0·7884	0·005541	67·62	0·9177	0·007563
15·11	0·8147	0·005863	79·00	0·9426	0·008095
29·40	0·8411	0·006226	89·73	0·9655	0·008861
42·91	0·8671	0·006622	100·00	0·9909	0·01010
55·60	0·8926	0 007068	—	—	—

Ethyl Alcohol and Anisole.

0·00	0·7879	0·01113	67·68	0·9167	0·009039
15·21	0·8147	0·01045	79·05	0·9415	0·009045
29·62	0·8405	0·009895	89·98	0·9660	0·009243
43·00	0·8665	0·009474	100 00	0 9960	0·01008
55·67	0·8918	0 009184	—	—	—

Methyl Alcohol and Phenetole.

Phenetole. Per cent.	Density.	Viscosity.
0·00	0·7879	0·005535
14·83	0·8107	0·005957
28·93	0·8331	0·006406
42·24	0·8555	0·006954
54·88	0·8771	0·007572
67·00	0·8987	0·00816
78·57	0·9212	0·00894
100·00	0·9622	0·01142

Ethyl Alcohol and Phenetole.

Phenetole. Per cent.	Density.	Viscosity.
0·00	0·7879	0·01113
14·97	0·8106	0·01067
28·89	0·8329	0·01035
42·32	0·8551	0·01010
54·97	0·8766	0·00997
67·05	0·8981	0·00991
78·50	0·9194	0·01000
90·25	0·9421	0·01035
100·00	0·9619	0·01135

Discussion of Results.

From the results given in the various tables and figures it appears obvious that in no case does the viscosity attain a maximum value, such as is observed in a number of cases of association in mixtures of liquids.

On the other hand, in nearly all cases there is a considerable departure from the calculated values, and in two cases a minimum value for the viscosity was observed.

These results indicate that when the associated alcohols are mixed with ethers, dissociation of the former takes place, and therefore the viscosity of the mixture is less than that calculated from the viscosity of the components.

The question next arises: "What part does the ether play in the process of dissociation?" At first sight it might appear that the ether merely acted as a diluent, displacing the equilibrium in the system $(\mathrm{R{\cdot}OH})^n \rightleftarrows n\text{-}\mathrm{R{\cdot}OH}$.

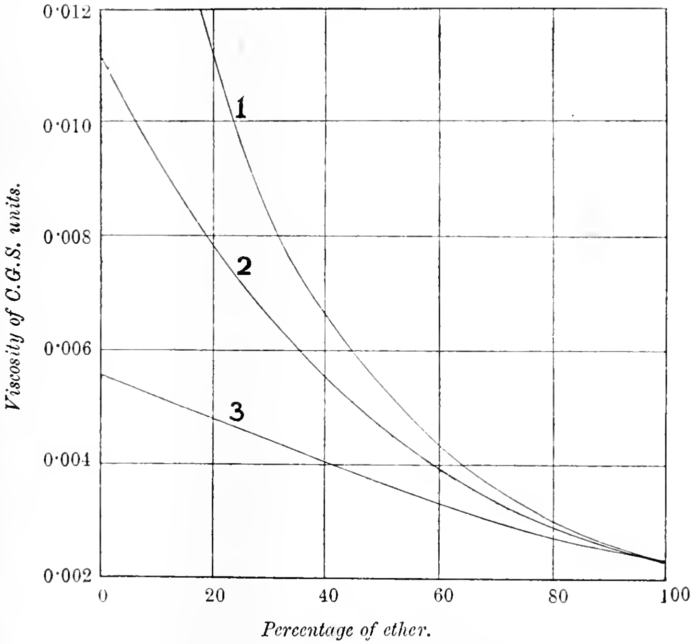
Such an assumption, although apparently justifiable by the present evidence, does not satisfactorily explain the various properties of these ether–alcohol solutions. The above-mentioned property of dissolving certain varieties of nitrocellulose could on this assumption be explained only by the supposition that the non-associated alcohol is a solvent for nitrocellulose, whilst the latter is insoluble in the associated liquids.

From this it would appear that any indifferent liquid when mixed with alcohol would form a nitrocellulose solvent, and, further, that the higher the degree of association of the alcohol the less would be its solvent power for nitrocellulose.

Neither of these deductions is correct, as it is well known that substances, other than ethers, which have no solvent power themselves for nitrocellulose do not in general form solvents for nitrocellulose when mixed with alcohols. Further, in the paraffin series of alcohols the degree of association decreases with increase of molecular weight (Ramsay and Shields, *Zeitsch. physikal. Chem.*, 1893, **12**, 433), but at the same time the solvent power for nitrocellulose of mixtures with ether decreases.

Again, it would appear from curve I, Fig. 1, that in the mixture of ether and methyl alcohol, the most associated of the alcohols, dissociation has taken place only to a slight extent; yet this mixture has a much higher solvent power for nitrocellulose than a mixture of ethyl alcohol and ether.

FIG. 1.



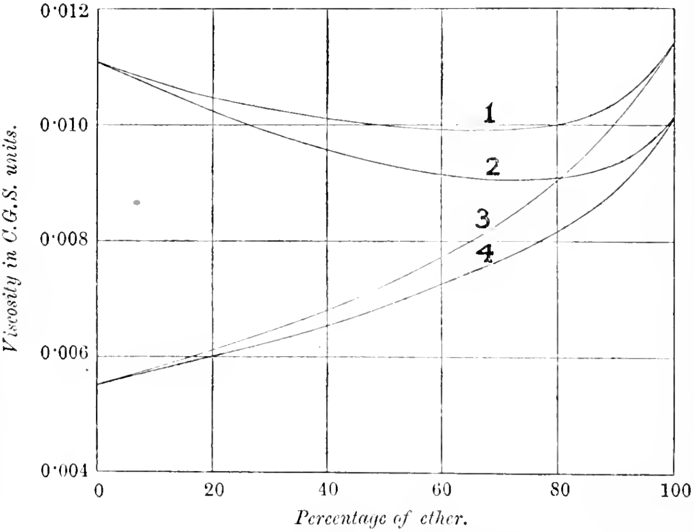
Percentage of ether.

Curve 1 : *Propyl alcohol and ethyl ether.*
,, 2 : *Ethyl* ,, ,, ,,
,, 3 : *Methyl* ,, ,, ,,

From these considerations it would appear highly probable that these mixtures of ether and alcohol contain an ether–alcohol complex, and there will thus be present in equilibrium a number of components, namely, non-associated ether, ether–alcohol complex, non-associated alcohol, and associated alcohol. To this ether–alcohol complex the solvent power of these mixtures for nitrocellulose may be ascribed. That the degree of association is greater at low temperatures than at higher, furnishes a probable explanation of the increased solubility of nitrocellulose in these mixtures at low temperatures (Berl and Klaye, *Zeitsch. Schiess. Sprengstoffwesen*, 1907, **2**, 381).

The shape of the viscosity curve must necessarily depend on the relative proportions of the components and on their internal frictions. If, for example, the complex had a high viscosity and were present in considerable amount, the mixture would give a curve showing a maximum. No case of this, however, has been observed with ether–alcohol mixtures; mixtures of alcohols and water probably owe their high viscosity to this cause.

FIG. 2.



Curve 1 : *Phenetole and ethyl alcohol.*
,, 2 : *Anisole* ,, ,,
,, 3 : *Phenetole and methyl alcohol.*
,, 4 : *Anisole* ,, ,,

If, however, the viscosity of the ether–alcohol complex were less or only slightly greater than that of the associated alcohol, it will readily be seen that the viscosity of the mixture would be less than that calculated from the viscosities of the ether and alcohol, and if these latter are not far removed from each other a curve with a minimum value would result.

From these considerations it would appear that, in general, no definite distinction is to be drawn between mixtures of liquids giving different types of viscosity-concentration curves; for example, in Fig. 2 it is seen that mixtures of phenetole and ethyl alcohol give a curve having a minimum value; but, on the other hand, mixtures of phenetole and methyl alcohol give no such minimum; but the values of the viscosities of these mixtures are obviously also below those calculated. The same is to be observed in the case of mixtures of anisole and methyl and ethyl alcohols, and, as there is no difference between methyl and ethyl alcohols which would justify an assumption that in this case the two are acting in different ways, it would certainly appear that the difference between the curves is due merely to the fact that the viscosity of ethyl alcohol is very little removed from those of anisole and phenetole.

From the study of the viscosities of mixtures at different temperatures, a similar conclusion has recently been drawn by Faust (*Zeitsch. physikal. Chem.*, 1912, **79**, 97).

These conclusions necessarily throw doubt on the applicability of the formula given by Lees (*loc. cit.*) for the viscosity of mixtures of liquids; thus calculation showed that this formula agreed approximately, although scarcely within the error of experiment, with results obtained in most cases; thus with anisole and methyl alcohol the following results were obtained. The third column gives the value of η calculated from the formula:

$$\eta^n = a\eta_1^n + (1-a)\eta_2^n \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a is the proportion by volume of the first component, and η_1 and η_2 their respective viscosities; n is a constant for each pair of liquids; in this case $n = -1{\cdot}3$.

Anisole by volume. Per cent.	η Found.	η Calculated.
0·00	0·005541	—
12·46	0·005863	0·005873
24·88	0·006226	0 006195
37·43	0·006622	0·006596
49·91	0·007068	(0·007068)
62·43	0·007563	0·007610)
74·96	0·008095	0·008288
87·45	0·008861	0·009114
100·00	0·01010	—

Thus, whilst in this case there is at least approximate agreement between the experimental and the calculated results, yet the mere substitution of ethyl alcohol for methyl alcohol results in a curve which cannot be expressed by the above formula, whatever value of n may be taken. This is obvious from the differentiation of the above expression.

$$\eta^n = a\eta_1^n + (1-a)\eta_2^n,$$

$$d\eta/da = 1/n(a\eta_1^n + \{1-a\}\eta_2^n)^{1/n-1}(\eta_1^n - \eta_2^n) \quad . \quad . \quad (2)$$

Examination of the right hand side of equation (2) shows, however, that the sign of $d\eta/da$ does not change as a changes from 0 to 1. In the last-mentioned case, namely, anisole and ethyl alcohol, however, the curve shows a minimum value for η, that is, $d\eta/da$ changes sign between the values $a=0$ and $a=1$; thus, it is impossible for Lee's equation to apply to this latter case.

In the same way, in the cases investigated by Faust (*loc. cit.*) a change in temperature is sufficient to cause a change from a curve which can be expressed approximately by Lees' formula to one which is incapable of being so expressed, and it may therefore be concluded that this formula is purely empirical and rests on no theoretical basis.

Conclusions.

(1) From the viscosity-concentration curves given by mixtures of ethers and alcohols it appears that dissociation of the latter takes place in such mixtures, but this dissociation is probably associated with the formation of an ether–alcohol complex, and to this complex the solvent power of these mixtures for nitrocellulose is due.

(2) No definite distinction can be made between viscosity-concentration curves showing maxima or minima and those in which the viscosities all lie between those of the two components.

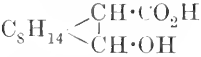
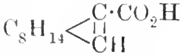
(3) The relation derived by Lees (*loc. cit.*) is purely empirical, and of strictly limited application.

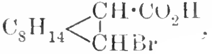
The author wishes to express his indebtedness to Col. Sir Frederic L. Nathan and to Messrs. Nobel's Explosives Co. for facilities for carrying out the above investigation, and also for permission to publish these results.

ARDEER.

CL.—*Contributions to the Chemistry of the Terpenes. Part XIII. The Preparation of Pure Bornylene.*

By GEORGE GERALD HENDERSON and WILLIAM CAW.

FOR the preparation of bornylene in quantity we have employed with satisfactory results Tschugaeff's method of converting borneol into methyl bornyl xanthate, and then decomposing the latter compound by the action of heat (*Ber.*, 1899, **32**, 3332). The yield is good, and the process involves no particular difficulty, but unfortunately one drawback attends its use. Until recently it was believed that bornylene obtained in this way is free from admixture with any isomeric terpene, but it is now evident, mainly as the result of Bredt's study of the borneol- and bornylene-carboxylic acids, that this is not the case. Starting with camphor, Bredt and Sandkuhl (*Annalen*, 1909, **366**, 11) produced bornylene by a series of reactions which appear to ensure the uniformity of the product. Camphorcarboxylic acid,  $C_8H_{14}\left<\begin{array}{l}CH\cdot CO_2H\\ \,|\\ CO\end{array}\right.$, was prepared from camphor, and when reduced electrolytically yielded two stereoisomeric borneolcarboxylic acids,  $C_8H_{14}\left<\begin{array}{l}CH\cdot CO_2H\\ \,|\\ CH\cdot OH\end{array}\right.$. By elimination of the elements of water these were converted into bornylenecarboxylic acid,  $C_8H_{14}\left<\begin{array}{l}C\cdot CO_2H\\ \,\|\\ CH\end{array}\right.$, from which, on treatment with hydrogen bromide, β-bromohydrobornylenecarboxylic acid,



$$C_8H_{14}\left<\begin{array}{l}CH\cdot CO_2H\\ \,|\\ CHBr\end{array}\right.$$

was obtained, and when heated with aqueous sodium carbonate this acid yielded a small quantity of bornylene, along with other products. Bornylene prepared in this way almost certainly contains no other isomeric terpene mixed with it, and differs considerably in its physical constants from Tschugaeff's preparation, which was formerly considered the pure hydrocarbon:

Bornylene.	Melting point.	Boiling point.	$[\alpha]_D$ in toluene.
Tschugaeff..........	103—104°	149°/750 mm.	13·77° (c=13·55)
Bredt..................	113°	146°/745 mm.	−21·69° (c=10·45)

In a later paper (*J. pr. Chem.*, 1911, [ii], **84**, 778) Bredt and Hilbing describe the production of a specimen of bornylene from β-iodohydrobornylenecarboxylic acid, which also melted at 113° and boiled at 146°, but had a somewhat higher specific rotation than former preparations, $[\alpha]_D$ −23·94° (in benzene, c=8·23).

Quite recently (*Annalen*, 1912, **388**, 260) Tschugaeff has shown that if methyl bornyl xanthate is decomposed slowly at as low a temperature as possible the bornylene produced is considerably purer than when the original method is employed, in which the temperature was allowed to rise up to or even above 220°. On heating the xanthate for a considerable time at 176—177° he obtained an excellent yield of a product which, after purification from traces of sulphur compounds by distillation over sodium, had the following constants: melting point, 105·5—106°; boiling point, 146·5—147·5°, $[\alpha]_D$ 15·06° (in toluene, c=20·19). This product was fractionated, and the portion which distilled below 147° was further purified by fractional distillation in alcohol vapour, precipitation from the distillate by addition of water, crystallisation from alcohol, and distillation over sodium, twice repeated, and ultimately an approximately pure specimen of bornylene was separated, which melted at 109—109·5°, boiled at 146·5/750 mm., and had $[\alpha]_D$ 19·29° (in toluene, $c = 12·75$).

It is evident from the facts quoted that bornylene, when prepared by Tschugaeff's method, contains a certain proportion of an isomeric terpene. In Bredt's opinion this impurity is camphene, but Tschugaeff could find no trace either of camphenic or of camphenilic acid among the products of the oxidation of this crude bornylene by dilute aqueous potassium permanganate, as would have been the case had camphene been present; whilst on the other hand he succeeded in isolating a small quantity (about 1 gram from 20 grams of crude bornylene, m. p. 103°) of a hydrocarbon, which had not been attacked by the oxidising agent, which melted at 64·5—65° and boiled at 153—153·5°, and therefore appeared to be cyclene. We hope that experiments which are in progress will help to settle this question.

Bredt's synthetic method, although affording a pure product, is unsuited for the preparation of bornylene in quantity on account of the smallness of the yield; thus, in the second paper quoted, it is stated that 7 grams of bornylene were obtained from 280 grams of the sodium salt of β-iodohydrobornylenecarboxylic acid. On the other hand, whilst the xanthate method of Tschugaeff gives an excellent yield, the bornylene produced is mixed with an isomeric terpene, and if it is purified according to the process described (*Annalen*, *loc. cit.*), only a small fraction of the original material is finally obtained, and even that is not quite pure. We therefore thought it desirable to seek for a method of purifying crude bornylene which would be satisfactory as regards both the quantity and the degree of purity of the product, and have now succeeded in meeting these requirements by employing a process of limited oxidation of the impure material with a strong solution of hydrogen peroxide.

In the course of a study of the action of hydrogen peroxide on bornylene, an account of which will be communicated to the Society before long, we observed that when crude bornylene was used the oxidising agent appeared to attack the impurity more rapidly than the bornylene itself. Accordingly several experiments were instituted in order to ascertain the most favourable proportion of hydrogen peroxide to be used, and, generally, the conditions under which the impurity could be removed with a minimum loss of bornylene by oxidation. As a result of these the following method was adopted:

Fifty grams of crude bornylene (m. p. 103°), prepared from the xanthate, after being distilled over sodium in order to remove the traces of sulphur compounds which it contains, were dissolved in 300 c.c. of glacial acetic acid, and 10 c.c. of a 30 per cent. aqueous solution of hydrogen peroxide were added. With these quantities about 1 molecule of hydrogen peroxide was present for 4 molecules of bornylene. The mixture was heated at 60—65° in a long-necked flask provided with an air condenser, and at intervals specimens of the crystals which had sublimed into the neck of the flask were removed and their melting point determined. The following melting points were found: After eight hours' heating, 106—110°; after sixteen hours, 107—111°; after twenty-four hours, 110—112°. As the melting point was not appreciably raised by continuing the heating for a longer period, the mixture was left to cool, and the crystalline solid which separated was collected, washed with dilute aqueous sodium carbonate and then with water, drained, and finally dried as completely as possible by pressure on a porous plate. A further quantity of bornylene was separated from the acid filtrate by addition of water, and after being washed and dried as just described, was found to be almost if not quite as pure as the first crop. The bornylene now melted at 111—112°, and was practically pure except for a small quantity of water, which is not easily removed on account of the tough, sticky nature of the hydrocarbon. When thoroughly dried by distillation over sodium, our specimen of bornylene was found to have practically the same constants as Bredt's pure product, having a melting point of 113°, boiling point of 146°/750 mm., and $[\alpha]_D^{20}$ $-22{\cdot}27°$ (in benzene, $c=8{\cdot}98$). The specific rotation was somewhat lower than that given by Bredt, but an examination of the *d*-borneol from which our specimen was prepared showed the presence of some *l*-borneol, which would account for the discrepancy. The specific refraction was determined in ethyl-alcoholic solution. Weight of substance $=1{\cdot}2744$, weight of solvent $=18{\cdot}6144$; D_4^{20} of solvent $=0{\cdot}7919$, of solution $=0{\cdot}7954$; n_D of solvent $=1{\cdot}36193$, of solution $=1{\cdot}36732$; molecular refraction found $=43{\cdot}38$; calculated for $C_{10}H_{16}|\overline{=}=43{\cdot}51$.

A second treatment of the purified bornylene with a small proportion of hydrogen peroxide produced no change in the melting point, and it therefore appears that the purification was complete. The yield was quite satisfactory, fully 60 per cent. of the crude material being obtained in this purified form.

In other experiments larger proportions of hydrogen peroxide than those given above were used, but the results were less favourable, for the oxidation of the impurity was not notably accelerated, whilst much larger quantities of the bornylene were also oxidised.

We also tried the effect of reducing the proportion of acetic acid, but again the result was disappointing, being solely a considerable increase in the time required to oxidise the impurity.

The only troublesome part of the process is the removal of the last traces of water from the bornylene. This is most easily effected by dissolving it in a small quantity of ether, adding sodium in sufficient quantity, expelling the ether, and distilling the residue. In working with bornylene its extraordinary volatility must always be borne in mind; thus when an ethereal solution is distilled a considerable quantity of the bornylene passes over with the ether vapour, and consequently the distillate should be preserved for use with fresh quantities of the material.

It is worth noting that we have found the yield of methyl bornyl xanthate to be considerably improved if in the first stage of the process, namely, the addition of carbon disulphide to a solution of the sodium derivative of borneol in toluene, at least three times the theoretical quantity of carbon disulphide is used.

We take this opportunity of expressing our thanks to the Research Fund Committee of the Carnegie Trust for a grant which defrayed the expense of this work.

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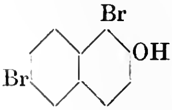
CLI.—*The Interaction of Bromine with the Two Sulphides of β-Naphthol.*

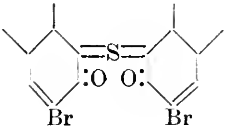
By Thomas Joseph Nolan and Samuel Smiles.

During the investigation of the relationship between the two sulphides of β-naphthol, the interaction of these substances with bromine was examined, and the products from either sulphide were found to be different. The difference between them was sufficiently remarkable to permit the hope that a more complete study of their nature would throw light on the constitution of the sulphides from which they were obtained; hence with this object in view the following experiments were made.

The stable sulphide of β-naphthol (m. p. 211°) readily reacts with bromine, yielding bromo-derivatives of β-naphthol, sulphur being eliminated in exchange for the halogen. As might be expected from a reaction of this nature there is some decomposition, but by employing three molecular proportions of the halogen to one of the sulphide, quite good yields of a dibromo-β-naphthol are obtained. This product is identical with that prepared by Armstrong and Rossiter (Proc., 1889, **5**, 71) from the interaction of bromine and β-naphthol. The same investigators showed that in this compound the substitution is heteronuclear, for on oxidation bromophthalic acid is obtained, and other circumstances lead to the conclusion that it is the 1:6-dibromo-derivative (I):



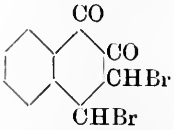
(I.)



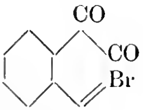
(II.)

When the unstable sulphide is treated with bromine under the same conditions, a substance is obtained in which the sulphur remains intact. Hydrogen bromide is abundantly liberated during the interaction, and the product contains three atomic proportions of bromine in the structure of the parental sulphide. Moreover, one of these halogen atoms is very easily removed as hydrogen bromide by cold pyridine or by solution in certain aqueous solvents, whilst a stable, crimson substance is formed. The fact that the latter compound furnishes phthalic acid on oxidation shows that the substitution is homonuclear, and further consideration of its general properties lead to the conclusion that it is the dibromonaphthasulphonium-quinone (II).

In order to obtain further proof of this structure for the compound, the interaction of bromine and β-naphthasulphonium-quinone was studied; but before describing the results obtained, some reference is necessary to the previous work of Zincke (*Ber.*, 1894, **27**, 2761) on the bromination of β-naphthaquinone. Zincke has shown that when β-naphthaquinone is treated with a molecular proportion of bromine, the orange-coloured additive product (III) is obtained,

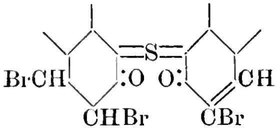


(III.)

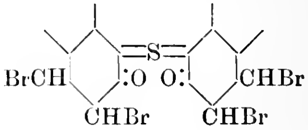


(IV.)

from which hydrogen bromide is easily removed, leaving the more stable bromo-β-naphthaquinone (IV). β-Naphthasulphonium-quinone shows a strictly analogous behaviour with bromine. On treating one molecular proportion of the quinone with two such proportions of bromine, complete interaction takes place, hydrogen bromide being liberated, and a sparingly soluble orange compound obtained. This contains three atomic proportions of bromine in the structure of the quinone, and it is identical with the product obtained from the interaction of bromine and the unstable sulphide. When viewed in the light of previous experience with β-naphthaquinone, the mode of formation and the ease with which this substance loses hydrogen bromide clearly indicate the following structure (V). It is also evident that the substance is formed by



(V.)



(VI.)

loss of hydrogen bromide from the tetrabromo-derivative (VI), which must occur at the initial stages of the interaction. There is nothing surprising in the spontaneous removal of hydrogen bromide in this manner, for Zincke (*loc. cit.*) has shown that dibromo-β-naphthaquinone readily suffers the same loss when dissolved in warm acetic acid; moreover, a second molecular proportion of the halogen acid is lost when the substance is warmed with aqueous acetone or acetic acid. The substance which is finally obtained must therefore be regarded as the dibromonaphthasulphonium-quinone (II), and, as previously remarked, confirmation of this result is afforded by the formation of phthalic acid on oxidation and by the general properties of the substance. The formulæ which are now used to illustrate the structure of this compound represent the halogen as occupying the 3:3′-positions, but it must be added that, beyond analogy to bromo-β-naphthaquinone, there is at present no independent reason for preferring this arrangement to the 4:4′-positions.

The two sulphides of β-naphthol are thus seen remarkably to differ in their reactions with bromine, and, since the results point to a profound difference in their constitutions, emphasis is given to the previous conclusion (Crymble, Ross, and Smiles, this vol., p. 1146) that these substances are not stereoisomerides.

The reactions described also afford further evidence of the nature of these sulphides. In a preliminary discussion it was remarked (Crymble, Ross, and Smiles, *loc. cit.*) that among other alternatives there existed the possibility that these sulphides might differ in the relative positions of the hydroxyl and thio-groups; but the facts now advanced render this explanation untenable. The situation of these groups in the stable sulphide (m. p. 211°) is clearly indicated by the mode of formation, the conversion into naphthathioxine, and by the fact that halogen or the benzeneazo-group on displacing sulphur enters the α-position of the naphthalene nucleus. Although both the stable and the unstable (153°) sulphides may be oxidised (see also Henriques, *Ber.*, 1894, **27**, 2999) to β-naphthasulphonium-quinone in alkaline solution, the circumstance cannot be regarded as proving the identity of position of the hydroxyl and thio-groups in either substance, for it is known that the unstable sulphide is converted into the stable by cold aqueous alkali hydroxide. The objection, however, cannot be raised against this conclusion from the present experiments, since with bromine the oxidation of the unstable sulphide takes place in an acid medium which does not effect the conversion.

It remains finally to remark on the general aspect of this contrast between the two sulphides. It is evident that in the stable compound the naphthalene nucleus behaves with respect to bromine similarly to that in β-naphthol, whilst in the unstable sulphide its behaviour resembles that in β-naphthaquinone. Whether in the latter case this difference is due to preliminary oxidation to the β-naphthasulphonium-quinone, must be decided by future experiments. These are now in progress.

EXPERIMENTAL.

Preparation of the Unstable Sulphide.—This substance was obtained by Henriques (*loc. cit.*) on reducing the sulphonium-quinone with zinc dust and acetic acid. We have found the following conditions to be suitable. The quinone, in quantities of 10 grams, is suspended in hot glacial acetic acid, and zinc dust is quickly added, the object being to effect reduction as rapidly as possible, since the product is gradually decomposed by boiling with this solvent. The crystalline mass of zinc salt is collected and suspended in boiling alcohol. Hydrochloric acid is then added to the mixture in sufficient quantity to decompose the salt; then after filtration the liquid is mixed with water until turbid. On cooling the liquid the required substance is precipitated in the crystalline state. The yield is usually about 7 grams.

Interaction of the Stable Sulphide (m. p. 211°) *with Bromine.*

Fifteen grams of bromine were gradually added to a mixture of 10 grams of the finely divided substance with cold glacial acetic acid. Interaction did not take place readily, but the sulphide gradually dissolved, and after the lapse of fifteen hours decomposition was complete at the atmospheric temperature. Water was then added, and the oil which separated was treated with aqueous alkali hydroxide. The alkaline solution was separated from the insoluble tarry material, and after being acidified was treated with a current of steam. The crystalline substance which collected in the distillate, after being purified by recrystallisation from alcohol with the addition of animal charcoal, was identified as the 2:6-dibromo-β-naphthol obtained by Armstrong and Rossiter (*loc. cit.*) from the interaction of bromine and β-naphthol. A sample of the substance melted at 106°, whether heated alone or mixed with the substance prepared by the last-named method. No other definite product could be isolated from this interaction, and the same product was obtained when two-thirds of this amount of bromine was used, the only difference being that the yields were somewhat smaller. The monobromo-derivative has not been observed as a product in this reaction.

Hydrogen Bromide Additive Product with Dibromonaphthasulphonium-quinone.

(*a*) *From β-Naphthasulphonium-quinone.*—Five grams of the quinone were suspended in about 40 c.c. of cold glacial acetic acid; then a solution of 5 grams of bromine in the same solvent was gradually added with continual shaking. The quinone dissolved and hydrogen bromide was liberated; after a brief interval an orange, crystalline substance was precipitated. This was collected and washed with a little acetic acid. The product was finally purified by adding water to a luke-warm solution in acetone until turbidity was produced, and then, after the lapse of a few minutes, the substance was precipitated in orange plates which melted at 167°. It may be remarked that the purification is not easily effected, for, if the heating with acetone be prolonged, bromo-derivatives of this solvent are formed, and if too much water be added, hydrogen bromide may be eliminated. The substance was identical in every respect with the product obtained in the following interaction. The yield was almost theoretical.

(*b*) *By Interaction of Bromine and the Unstable Sulphide* (153°).—Three grams of bromine were gradually added to 2 grams of the sulphide suspended in glacial acetic acid. The solid material dissolved, and subsequently an almost quantitative yield of the required substance crystallised from the reacting mixture. The product was collected and purified as described above. It melted at 167°, whether heated alone or mixed with the substance obtained from β-naphthasulphonium-quinone:

0·1052 gave 0·1671 CO_2 and 0·0178 H_2O. C=43·3; H=1·9.
0·1297 „ 0·1310 AgBr. Br=43·3.
$C_{20}H_{11}O_2Br_3S$ required C=43·2; H=2·0; Br=43·2 per cent.

When pure this substance is moderately stable, but when dissolved in organic media of basic character it quantitatively loses hydrogen bromide; the same decomposition occurs, although more slowly and not so completely, when aqueous organic media are employed, or if the solution in cold glacial acetic acid be kept.

Dibromonaphthasulphonium-quinone.

This substance may be prepared by removal of hydrogen bromide from the tribromo-derivative which is described in the foregoing section. The process may be effected by several reagents, of which two examples are given.

(*a*) *With Pyridine.*—The tribromo-derivative was dissolved in cold pyridine, and the red solution was poured into excess of aqueous sulphuric acid. After being collected, washed, and dried, the product was dissolved in tetrachloroethane. Ether was added to this solution until a turbidity was produced, and subsequently the dibromo-quinone was almost completely precipitated in the crystalline state. It was collected and thoroughly washed with ether to remove tetrachloroethane.

(*b*) *With Alkali Carbonate.*—A mixture of the tribromo-derivative and excess of potassium carbonate was treated for one hour with boiling acetone to which one-third of the bulk of water had been added. The insoluble product was purified as described.

The same substance may be directly prepared from β-naphthasulphonium-quinone by the interaction of equal weights of that compound and bromine in hot glacial acetic acid, for on heating in this solvent the tribromo-derivative loses hydrogen bromide. The substance is readily soluble in tetrachloroethane or pyridine, and sparingly so in cold acetone or acetic acid. It crystallises from a boiling solution in the latter solvent in dark red needles which melt at 193°:

0·1040 gave 0·1921 CO_2 and 0·0235 H_2O. C = 50·37; H = 2·5.
0·1241 ,, 0·0982 AgBr. Br = 33·6.
$C_{20}H_{10}O_2BrS$ requires C = 50·6; H = 2·1; Br = 33·7 per cent.

Like the parent quinone this bromo-derivative is not attacked by cold aqueous alkali hydroxide; it may be reduced by sodium ethoxide in alcoholic solution or by zinc dust in acetic acid; the product shows the characteristics of a hydroxy-compound, and it may be reoxidised to a quinone by alkaline ferricyanide.

β-Naphthaquinone is readily attacked by aniline (Liebermann and Jacobsen, *Annalen*, 1882, **211**, 75; Zincke, *Ber.*, 1881, **14**, 1494), yielding the 4-anilino-derivative, and a similar behaviour has been observed with 3-bromonaphthaquinone (Brömme, *Ber.*, 1888,

21, 390). The sulphonium-quinones behave in a similar manner, but they are less reactive than the simpler analogues, since the hot reagent is necessary to effect the interaction.

A solution of the dibromosulphonium-quinone in aniline was warmed for a few minutes, and then poured into excess of dilute aqueous hydrogen chloride. The brown, insoluble material was collected and washed with hot acetone, which removed resinous material. The yellow residue was purified by adding ether to the concentrated solution in aniline; the substance is then obtained in small, yellow needles, which melt at 238°. Analysis and investigation of the properties of the compound, which is insoluble in alkali hydroxide, indicate that it is more complex than the simple aniline derivative which might be expected. The complete examination of this substance has therefore been deferred until the nature of the product obtained from β-naphthasulphonium-quinone has been determined.

Phenylhydrazine readily reacts with this bromoquinone when warmed with it in acetic acid. In this case, also, the product is more complex than the simple hydrazone which is given by naphthasulphonium-quinone, and it appears that besides reacting with the carbonyl groups, this reagent attacks other groups in the molecular structure.

Oxidation of Dibromonaphthasulphonium-quinone.

Ten grams of the quinone were suspended in an aqueous solution of alkali hydroxide, to which an excess of potassium permanganate was added. The mixture was heated at about 90° for two days, and the insoluble material was then removed. From this about half of the original substance was recovered unchanged, whilst from the alkaline liquid 1 gram of phthalic acid was isolated. This acid was identified by the equivalent and by the melting point of a mixture with phthalic acid compared with a pure sample of that substance heated under the same conditions.

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CLII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part III. The Rotations of* ac-*Tetrahydro-2-naphthol and Some of its Esters.*

By ROBERT HOWSON PICKARD and JOSEPH KENYON.

ac-TETRAHYDRO-2-NAPHTHOL, first described by Bamberger and Lodter (*Ber.*, 1890, **23**, 205), has been resolved into its optically active components by one of us and Littlebury (Trans., 1906, **89**, 467). The operations carried out in the process were (*a*) the conversion of the reduced naphthol into the corresponding *l*-menthylcarbamates, (*b*) the fractional crystallisation of these esters, and (*c*) the separate hydrolysis of the least and most soluble esters. It has been pointed out (*inter alia*, Trans., 1907, **91**, 1974) that such a process is not very satisfactory, as generally it does not allow of the preparation of the two optically active isomerides in a state of purity. We have therefore resolved this alcohol by the method used for the other alcohols described in this investigation (Part I., Trans., 1911, **99**, 45; Part II., this vol., p. 620). This resolution is apparently complete, for the dextrorotatory and the lævorotatory isomerides obtained from the least soluble brucine and cinchonidine salts respectively of the hydrogen phthalate crystallise readily, melt at 50°, and have specific rotatory powers, $[\alpha]^{20}_{D} \pm 75{\cdot}2^{\circ}$ in the supercooled state, or $[\alpha]_{D} \pm 67{\cdot}1^{\circ}$ in 5 per cent. chloroform solution, whereas the product of highest rotatory power previously obtained (*loc. cit.*) had $[\alpha]_{D} + 28{\cdot}2^{\circ}$ in chloroform solution, and was an oil. Equal amounts of the *d*- and *l*-crystals reduced to a state of powder rapidly coalesce at the ordinary temperature to an oil, whilst all experiments to bring about a solidification of the optically inactive product at temperatures down to -20° were unsuccessful.

Dr. A. E. Dunstan and Mr. F. B. Thole have very kindly determined the viscosities of the dextroisomeride and of a mixture of equal amounts of that and the lævoisomeride. The viscosities of these at temperatures between 30° and 60° (the dextroisomeride having been examined in the supercooled state) were found by them to be identical, so that it would appear (compare Trans., 1910, **97**, 1251) that the optically inactive *ac*-tetrahydro-2-naphthol is a *dl*-mixture, and not a true racemate.*

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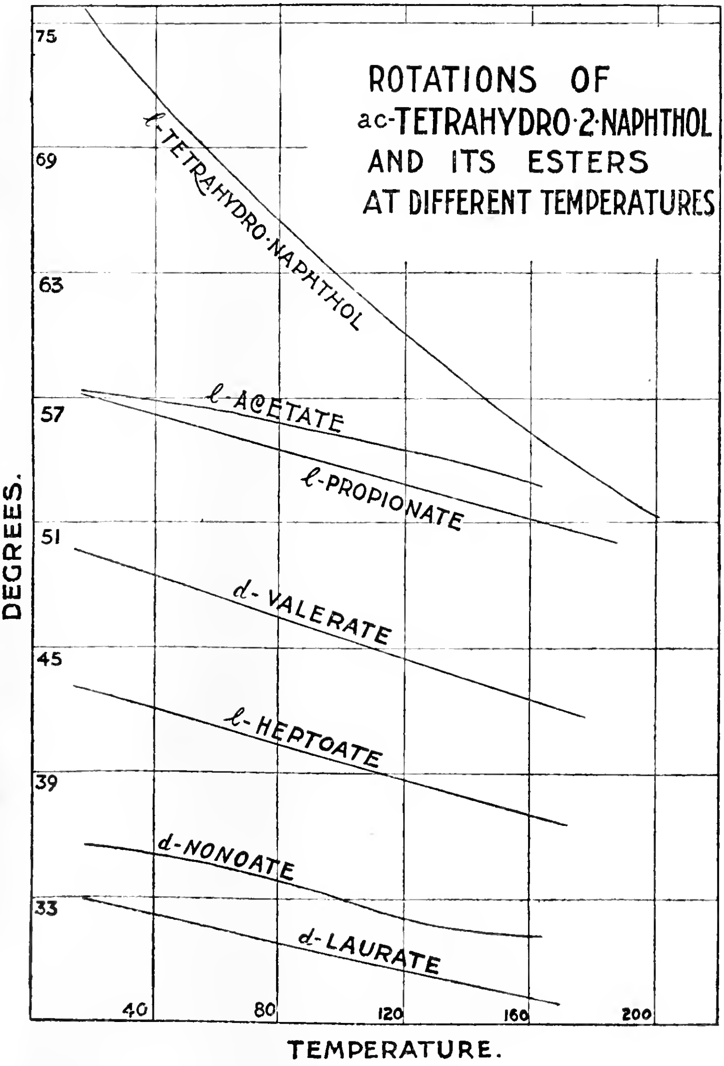
* In Parts I and II (*loc. cit.*) the authors have several times written in a somewhat loose form of expression of the racemic alcohols, although the existence of a racemic liquid is still perhaps an open question. Messrs. Dunstan and Thole are undertaking the determination of the viscosities of the other optically active alcohols already prepared by the authors.

Being in possession of a quantity of an alcohol with a considerable rotatory power and of high molecular weight, and, moreover, one which contains only one asymmetric carbon atom, the authors have taken the opportunity to test the validity of the views put forward some years ago by P. F. Frankland (see also Presidential Address, this vol., p. 659) as to the rotatory powers of a series of homologous compounds. In these it is suggested that from stereochemical considerations a change in the regularity of the molecular rotatory powers of the members of a homologous series may be expected to occur when the growing chain contains five or six carbon atoms, that is, at the point when a continuous chain of carbon atoms may be expected to all but return upon itself. As, however, the change in the regularity of the rotatory powers, such as, for example, the attainment of a maximum or constant rotation, if resulting from such steric interference, would always be exhibited by (or at) the member of the series containing five or six carbon atoms, Frankland further suggested that the other groups, which are present in the molecule, may interfere with the normal development of the homologous chain, and therefore cause the maximum (or constant) rotation to be exhibited by a member of the series containing fewer or more than five carbon atoms. These views were put forward after consideration of several series of compounds, each of which was composed of derivatives of some one optically active compound, and in all of which the growing chain was not directly attached to the asymmetric carbon atom. The authors have recently described (*loc. cit.*) two series, which are not composed of derivatives of a single optically active compound, but of some ten and eight independent compounds respectively, and in all the members of which the growing chain is attached directly to the asymmetric carbon atom. The rotatory powers of the members of these two series apparently do not exhibit the regularities to be expected from this hypothesis of Frankland; thus in the series $CH_3 \cdot CH(OH) \cdot R'$ the values of the molecular rotatory powers (at the boiling point) continually increase—at least, up to that of the member with R′ containing eleven carbon atoms, and certainly shows no break in the regularity of the increase in rotatory power at the amyl or hexyl member, whilst in the series

$$(CH_3)_2CH \cdot CH(OH) \cdot R'$$

the rotatory power attains a maximum (and possibly a constant) value when R′ contains a greater number of carbon atoms than the *iso*propyl group, that is, when R′ = *n*-butyl. It appeared, therefore, of interest to compare the values of the molecular rotatory power of the members of a series of esters of *ac*-tetrahydro-2-naphthol with normal fatty acids, for since two of the valencies of the asymmetric carbon atom are attached to the same group, steric interference with the homologous chain might be small. It will be seen, however, from table I that the values of molecular rotatory

Specific rotatory powers at different temperatures.



powers continuously decrease from that for the propionate term to that for the *n*-nonoate, whilst the value for the laurate term is higher than that for the nonoate. The influence of temperature on the specific rotatory powers of the alcohol and its esters has also been investigated, the results being shown in the diagram. It will be seen that the curves illustrating this influence of temperature are very similar in the case of all the esters, except of the nonoate. This phenomenon shows a striking contrast to the results obtained (*loc. cit.*) for the *n*-propyl member of the *iso*propyl series, for which a "temperature–specific rotatory power" curve was obtained different in shape from the approximately parallel ones obtained for all the higher members of this series; thus the values of the molecular rotatory powers of the three series so far described by the authors do not seem to fit in with Frankland's hypothesis, but further discussion of this should be reserved until more material is available, and the influence of temperature on the rotatory power of the members of such homologous series more carefully investigated.

TABLE I.

Esters of *ac*-tetrahydro-2-naphthol.	$D_{4^\circ}^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.	$[\alpha]_D^{160^\circ}$.	$[M]_D^{160^\circ}$.
Acetate	1·0891	57·5°	109·2	53·2°	101·1
Propionate	1·0640	57·0	116·2	51·3	104·7
n-Valerate	1·0281	49·0	113·7	42·5	98·8
n-Heptoate	1·0034	42·9	111·5	36·9	95·9
n-Nonoate	0·9805	35·4	102·0	31·1	89·6
Laurate	0·9645	32·7	107·9	28·1	92·7

It is noteworthy that the densities of all these esters, except that of the nonoate, when plotted against molecular weight, lie on a smooth curve.

EXPERIMENTAL.

Resolution of ac-*Tetrahydro-2-naphthol.*

The general experimental details of the resolution were similar to those for the resolutions of the alcohols described in Parts I and II (*loc. cit.*). *ac*-Tetrahydro-2-naphthol (Bamberger and Lodter, *Ber.*, 1890, **23**, 205) was converted into the hydrogen phthalate by heating with phthalic anhydride at 115° for twelve hours. The *ester* crystallises readily from a mixture of benzene and light petroleum in large prisms, which melt at 90—92°. When titrated with a solution of sodium hydroxide, 0·1683 was neutralised by 0·0225 NaOH, the calculated amount for $CO_2H \cdot C_6H_4 \cdot CO_2 \cdot C_{10}H_{11}$ being 0·0227 NaOH.

The *cinchonidine* salt of the hydrogen phthalate of *l*-*ac*-tetrahydro-2-naphthol is readily separated from the salt of the corresponding dextrorotatory ester by crystallisation from acetone. The mixture of the two salts separates from acetone containing a little chloroform in clusters of very fine, hair-like needles, which melt at 152—155°. After five recrystallisations from acetone the separation of the two salts is complete. The cinchonidine salt of the *l*-ester melts at 168—169°, and when observed in the polarimeter gave the following result:

1·0034, made up to 20 c.c. with ethyl alcohol, gave $\alpha - 7·14°$, whence $[\alpha]_D$ $-71·16°$.*

The solubility of this pure *lBlA*-salt is very small in acetone. In the separation described above 100 grams of the product obtained after the second recrystallisation requires about 5 litres of hot acetone for its solution. The fractional crystallisation was also carried out, using ethyl alcohol as the solvent. This is more convenient as the required salt is more soluble in it, but the separation is not so rapid.

The hydrogen phthalate obtained from the first two mother liquors of the cinchonidine salts was converted into the *brucine* salt. The product crystallised readily from acetone, in which it is fairly soluble, and after nine recrystallisations yields, in an indefinite crystalline form, the pure *lBdA*-salt, which melts at 109—112°:

1·0445, made up to 20 c.c. with ethyl alcohol, gave $\alpha + 0·50°$, whence $[\alpha]_D$ $+4·79°$.

The *l*- and *d*-hydrogen phthalates, prepared in the manner previously described (*loc. cit.*) from the pure cinchonidine and brucine salts respectively, crystallise in needles from a mixture of benzene and light petroleum, and melt at 94—96°.

The following polarimetric observations were made:

l-*Ester:*

1·0931, made up to 20 c.c. with chloroform, gave $\alpha - 1·50°$, whence $[\alpha]_D$ $-13·72°$.

0·9615, made up to 20 c.c. with ethyl alcohol, gave $\alpha - 0·93°$, whence $[\alpha]_D$ $-9·67°$.

d-*Ester:*

0·8886, made up to 20 c.c. with chloroform, gave $\alpha + 1·19°$, whence $[\alpha]_D$ $+13·39°$.

1·0040, made up to 20 c.c. with ethyl alcohol, gave $\alpha + 0·98°$, whence $[\alpha]_D$ $+9·76°$.

The pure esters were separately hydrolysed in the usual manner, the alcohols being removed by a current of steam, extracted with ether, and distilled under diminished pressure. They boil at 141°/17 mm., rapidly set when cold to a hard, crystalline mass, and crystallise from light petroleum in large, prismatic needles, which melt at 50°. The following polarimetric observations were made:

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* All polarimetric observations of solutions recorded in this paper were made in a 2-dcm. tube.

l-ac-*tetrahydro-2-naphthol,* 0·9600, made up to 20 c.c. with chloroform, gave α $-6{\cdot}44°$, whence $[\alpha]_D$ $-67{\cdot}1°$.

d-ac-*tetrahydro-2-naphthol,* 1·0188, made up to 20 c.c. with chloroform, gave α $+6{\cdot}84°$, whence $[\alpha]_D$ $+67{\cdot}1°$.

l-ac-*Tetrahydro-2-naphthyl phenylcarbamate* is formed when equivalent amounts of the *l*-alcohol and phenylcarbimide are mixed and allowed to remain at the ordinary temperature for twelve hours. It separates from dilute ethyl alcohol in feathery needles, which melt at 119°:

1·0680, made up to 20 c.c. with chloroform, gave α $-2{\cdot}81°$, whence $[\alpha]_D$ $-26{\cdot}31°$.

1·0135, made up to 20 c.c. with benzene, gave α $-3{\cdot}34°$, whence $[\alpha]_D$ $-32{\cdot}95°$.

Esters of l- *and* d-ac-*Tetrahydro-2-naphthols.*

These esters were in each case prepared by heating the alcohol with a slight excess of the anhydride * of the acid at 110—120° for six hours. The mixture was then poured into a solution of sodium carbonate, and after some time the ester was extracted with ether and distilled under diminished pressure. The following were obtained as strongly refractive oils with slight, but fragrant, odours: l-ac-*tetrahydro-2-naphthyl acetate,* b. p. 149°/18 mm.; l-ac-*tetrahydro-2-naphthyl propionate,* b. p. 158—159°/18 mm.; d-ac-*tetrahydro-2-naphthyl* n-*valerate,* b. p. 169°/11 mm.; l-ac-*tetrahydro-2-naphthyl* n-*heptoate,* b. p. 191—193°/14 mm.; d-ac-*tetrahydro-2-naphthyl* n-*nonoate,* b. p. 195—197°/5 mm.; and d-ac-*tetrahydro-2-naphthyl laurate,* b. p. 218°/3 mm. When cold the last sets to a crystalline mass, which melts at 35—36°. The purity of the ester in each case was proved by (*a*) the estimation of the amount of sodium hydroxide required for the hydrolysis, and (*b*) the determination of the specific rotatory power of the alcohol obtained in the hydrolysis.

Below are given the results of the determinations at various temperatures of the density and rotatory power of the compounds, the densities having been determined in a pyknometer holding about 1·5 c.c., and the rotatory powers in a jacketted polarimeter tube 50 mm. long.

l-ac-Tetrahydro-2-naphthol: $D_{4°}^{61°}$ 1·0589, $D_{4°}^{96°}$ 1·0309, $D_{4°}^{129°}$ 1·0009, and $D_{4°}^{155°}$ 0·9778. Observed rotations for 50 mm.: α_D^{19} $-41{\cdot}33°$ (in

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* n-*Valeric anhydride* does not seem to have been described previously. It is readily obtained by heating a mixture of the sodium salt and the chloride of *n*-valeric acid. It is a mobile, colourless liquid, which boils at 218°/754 mm. and has $D_{4°}^{17°}$ 0·9223.

supercooled state), α_{D}^{90} −33·10°, α_{D}^{121} −30·24°, α_{D}^{137} −28·89°, α_{D}^{159} −27·17°, α_{D}^{172} −26·16°, α_{D}^{183} −25·18°, and after cooling, α_{D}^{40} −38·62°.

l-ac-Tetrahydro-2-naphthyl acetate: $D_{4^\circ}^{14^\circ}$ 1·0926, $D_{4}^{51^\circ}$ 1·0648, $D_{4}^{90^\circ}$ 1·0271, and $D_{4^\circ}^{131}$ 0·9914. Observed rotations for 50 mm.: α_{D}^{15} −31·40°, α_{D}^{54} −29·97°, α_{D}^{94} −28·40°, α_{D}^{130} −26·93°, and α_{D}^{460} −25·64°.

l-ac-*Tetrahydro-2-naphthyl propionate:* $D_{4^\circ}^{16^\circ}$ 1·0675, D_{4}^{48} 1·0404, $D_{4^\circ}^{91^\circ}$ 1·0027, and $D_{4^\circ}^{128^\circ}$ 0·9698. Observed rotations for 50 mm.: α_{D}^{21} −30·28°, α_{D}^{56} −28·76°, α_{D}^{94} −27·09°, α_{D}^{127} −25·58°. and α_{D}^{168} −23·81°.

d-ac-*Tetrahydro-2-naphthyl* n-*valerate:* $D_{4}^{16^\circ}$ 1·0317, $D_{4}^{56^\circ}$ 1·0029, $D_{4^\circ}^{88^\circ}$ 0·9790, and $D_{4^\circ}^{133^\circ}$ 0·9486. Observed rotations for 50 mm.: α_{D}^{21} +25·23°, α_{D}^{34} +24·79°, α_{D}^{92} +22·43°, α_{D}^{118} +21·42°, and α_{D}^{156} +19·98°.

l-ac-*Tetrahydro-2-naphthyl* n-*heptoate:* $D_{4^\circ}^{15^\circ}$ 1·0071, $D_{4^\circ}^{48^\circ}$ 0·9846, $D_{4^\circ}^{92^\circ}$ 0·9529, and $D_{4^\circ}^{135^\circ}$ 0·9241. Observed rotations for 50 mm.: α_{D}^{19} −21·58°, α_{D}^{53} −20·46°, α_{D}^{84} −19·19°, α_{D}^{119} −18·25°, and α_{D}^{144} −17·30°.

d-ac-*Tetrahydro-2-naphthyl* n-*nonate:* $D_{4^\circ}^{18^\circ}$ 0·9821, $D_{4^\circ}^{58^\circ}$ 0·9555, $D_{4^\circ}^{96^\circ}$ 0·9282, and $D_{4^\circ}^{138^\circ}$ 0·9005. Observed rotations for 50 mm.: α_{D}^{20} +17·37°, α_{D}^{62} +16·39°, α_{D}^{100} +15·14°, α_{D}^{128} +14·45°, α_{D}^{156} +13·88, and after cooling, α_{D}^{52} +33·28°.

d-ac-*Tetrahydro-2-naphthyl laurate:* $D_{4^\circ}^{17^\circ}$ 9·9677, $D_{4^\circ}^{56^\circ}$ 0·9419, $D_{4^\circ}^{90}$ 0·9180, and $D_{4^\circ}^{136^\circ}$ 0·8896. Observed rotations for 50 mm. · α_{D}^{20} +15·77°, α_{D}^{38} +15·34°, α_{D}^{65} +14·71°, α_{D}^{85} +14·13°, α_{D}^{116} +13·27°, α_{D}^{144} +12 65°, α_{D}^{162} +12·21°, and α_{D}^{184} +11·69°.

The authors have much pleasure in acknowledging the able assistance given to them by Mr. William Osbaldiston, who has prepared the large amount of the tetrahydronaphthol required; and further, desire to express their thanks to the Government Grant Committee for a grant, which has defrayed some of the expense of this investigation.

MUNICIPAL TECHNICAL SCHOOL,
BLACKBURN.

CLIII.—*The Essential Oil of the "Nepal Sassafras" or "Nepal Camphor" Tree.*

By SAMUEL SHROWDER PICKLES.

Cinnamomum glanduliferum, Meissn., the "Nepal Camphor wood," or "Nepal Sassafras," is a large tree occurring in the Southern Himalaya from Kumaon eastwards to Assam, especially in Nepal.

The wood of the tree is pale brown, durable, easily worked, and not attacked by insects. It is used in Assam for boat-building and for making boxes. When freshly cut, the wood is highly scented, and its odour has been described as camphoraceous. In India it has been used as a substitute for sassafras.

A specimen of camphor, reported to have been obtained from the leaves of this tree by R. S. Pearson, was recently identified by Schimmel & Co. as *d*-camphor (Semi-annual Report, October, 1910, p. 145).

The volatile constituents of the wood do not appear to have been investigated, although all references to the tree as perfume-yielding are made with regard to the wood, and not to the leaves, etc.

Some time ago a consignment of the wood was received at the Imperial Institute from the Government of India. The specimen was said to come from Bishnath, Assam, where the tree yielding it is called "gonserai," and this paper relates to an investigation of the essential oil of this tree, which has been conducted in the Scientific and Technical Department of the Imperial Institute.

The camphor wood or sassafras trees of Northern India were apparently formerly regarded as *C. glanduliferum*, but the species occurring in Assam and Darjeeling is now considered to be the closely related *C. cecicodaphne*, Meissn. ("Indian Timbers," Gamble, 1902, 563; see also Brandis, "Indian Trees," 1906, 534).

In the "Dictionary of Economic Products of India" (1889) Watt makes no mention of the latter tree, and under *C. glanduliferum* includes the tree having the native names "rohu" and "gunserai" (gonserai?). In the same author's "Commercial Products of India," published in 1908, however, the statement occurs that *C. glanduliferum* is readily confused with *C. cecicodaphne*, Meissn. (the "rohu" and "gunserai"), a tree of the Eastern Himalaya, especially Darjeeling and Assam.

In the present instance the name *C. glanduliferum* as applied to the wood under examination is possibly used in its older and wider significance.

Extraction and Yield of Oil.

The material from which the oil was obtained consisted of billets of heart wood free from bark. It was reddish-brown, and had an odour more safrole-like than camphoraceous. For the extraction of the oil the wood was first ground, and afterwards submitted to steam distillation. During the process of grinding, the material suffered a considerable decrease in weight, due principally to loss of moisture, 105 lbs. of wood yielding 74 lbs. 7 ozs. of ground material. The weight of oil obtained after drying and filtering amounted to 3 lbs. 1½ ozs., being a yield of 2·95 per cent. on the original material, or 4·16 per cent. on the wood after grinding.

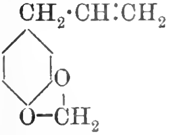
General Characters of the Oil.

The clear, pale yellow oil possesses an odour resembling that of safrole with, however, a suggestion of anise. It has the following general characters: D_{15}^{15} 1·1033; $\alpha_D^{20^\circ}$ (in 1-dcm. tube) $-0^\circ 4'$; saponification value 2·8; saponification value, after acetylation, 7·0.

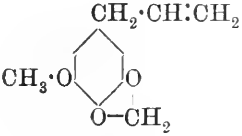
It is soluble in half its volume of 90 per cent. alcohol, and in five volumes or more of 80 per cent. alcohol.

The chemical examination of the oil has revealed certain peculiarities in composition, which appear to be of considerable interest. In the first place, there are no terpenes present, and acids, alcohols, esters, aldehydes, and ketones are either absent or are present only in very small quantity.

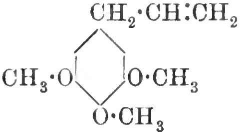
The oil consists almost entirely of ethers, and the nature of these demonstrates in a remarkable manner the capacity of certain plants for producing different chemical compounds of a similar type. The three compounds which constitute the bulk of the oil are the following:



(I.)
Safrole.



(II.)
Myristicin.



(III.)
Elemicin.

Safrole is the principal constituent of sassafras oil, myristicin of the essential oils of mace and of nutmeg, whilst elemicin has recently been discovered by Semmler (*Ber.*, 1908, **41**, 1768) in elemi oil.

Chemical Examination.

It is evident from a consideration of the chemical and physical constants given above that free acids, esters, phenols, and alcohols constitute a very small proportion of the total oil. In a preliminary experiment on a small scale, the oil was found to distil almost completely between 245° and 280°, although on redistillation of the fractions of lower boiling point a considerable portion was found to boil between 233° and 240°.

Since no fraction of the oil boils below 230°, the absence of terpenes can safely be presumed, and on examining the oil for aldehydes by agitating a portion with a strong solution of sodium hydrogen sulphite and subsequently treating the aqueous solution with sodium carbonate, a negative result was obtained.

It was therefore concluded that the oil consisted mainly of a mixture of ethers. A methoxyl determination was made, the method used being that of Zeisel as modified by Perkin (Trans., 1903, **83**, 1367), with the following result:

0·4600 gave 0·5635 AgI. OMe = 16·16 per cent.

The presence of safrole in the portions of the oil of lower boiling point was suggested by the odour of the distillate, but as safrole contains no methoxyl group the above figure indicates the presence in the oil of other constituents comparatively highly methoxylated.

Distillation of the Oil.

For the chemical examination 500 c.c. of the oil were taken, and this was first separated into about equal proportions by distillation under diminished pressure. The portion of lower boiling point was then cooled in a freezing mixture, seeded with a crystal of pure safrole, and afterwards left in an ice-chest for twenty-four hours.

A quantity of crystalline material had then separated in broad, prismatic crystals, having the characteristic odour of safrole (fraction 1), and the remaining liquid was drained off.

After the separation of the crystals the remaining oil was fractionally distilled, the portion of lower boiling point under atmospheric pressure and that boiling higher, under diminished pressure. The oil was finally separated into the following fractions:

Fraction (1).—Oil obtained from the crystalline material, which melted at +9° to a colourless liquid, 57 c.c.; (2) b. p. 233—238°, 37 c.c.; (3) b. p. 238—243°, 55 c.c.; (4) b. p. 243—248°, 29 c.c.; (5) b. p. 248—253°, 20 c.c.; (6) b. p. 253—258°, 18 c.c.; (7) b. p. 132—137°/12 mm., 16 c.c.; (8) b. p. 137—142°/12 mm., 22 c.c.; (9) b. p. 142—147°/12 mm., 25 c.c.; (10) b. p. 147—152°/12 mm., 57 c.c.; (11) b. p. 152—157°/12 mm., 89 c.c.; (12) b. p. 157—162°/12 mm., 57 c.c.; (13) b. p. 162—172°/12 mm., 11 c.c.; residue and loss, 7 c.c. Total = 500 c.c.

An examination of the distillation results shows that the oil consists in the main of two chief fractions boiling (1) below 243°, and (2) at 147—162°/12 mm.

As, except in the case of the fraction of lower boiling point, the characters (odour, etc.) of the distillate gave no clue to their composition, it was necessary to analyse and examine each fraction separately.

Fraction (1), obtained from the crystalline material, which separated on cooling the oil. The liquid possessed a strong odour of safrole. D^{15} 1·1059, α_D 0°0′:

0·2330 gave 0·6340 CO_2 and 0·1280 H_2O. C = 74·2; H = 6·1.

$C_{10}H_{10}O_2$ requires C = 74·1; H = 6·2 per cent.

The liquid solidified in a freezing mixture to a crystalline mass, which melted again at +9°.

A methoxyl determination showed that this fraction, although not quite free from methoxy-compounds, contained so little that they could be treated as minor impurities.

Identification of Safrole.

(1) *Preparation of Piperonal.*—The above properties are practically those of pure safrole, and the identity with this compound was proved by the formation of the well-known derivatives piperonal and safrole α-nitrosite.

A small quantity (5 grams) of this fraction was treated with chromic acid mixture, first in the cold, and then warmed on the water-bath, with frequent shaking. After cooling, the mixture was extracted with ether, the ethereal solution washed, first with water, and then with sodium carbonate solution. On evaporation of the ether, a brown oil remained, from which, by extracting with sodium hydrogen sulphite solution and subsequent neutralisation of the aqueous solution, a viscid, colourless liquid was obtained. This, on keeping, solidified completely to a crystalline mass. It had the characteristic, pleasant odour of piperonal, and melted sharply at 37°.

(2) *Preparation of Safrole α-Nitrosite.*—To an aqueous solution of sodium nitrite in a small flask was added a solution of the oil (5 grams) in light petroleum. Dilute sulphuric acid was added gradually to the mixture, and after some time a yellow, amorphous solid separated. The latter was collected, washed with dilute potassium hydroxide, and then successively with water, alcohol, and ether. The nitrosite was dried on a porous plate, and was then obtained as a pale yellow, sandy powder, melting at 130—131°. The melting point of safrole α-nitrosite is stated to be 129—130°.

Fraction No. 2, b. p. 233—238°. D^{15} 1·0930:

0·1610 gave 0·4355 CO_2 and 0·0925 H_2O. C = 73·8; H = 6·4.
0·3530 ,, 0·036 AgI. OMe = 1·35.
$C_{10}H_{10}O_2$ requires C = 74·1; H = 6·2 per cent.

Fraction No. 3, b. p. 238—243°. D^{15} 1·1025.

0·1645 gave 0·4460 CO_2 and 0·0945 H_2O. C = 73·94; H = 6·4.
0·3060 ,, 0·065 AgI. OMe = 2·80.

Fractions 2 and 3 also consisted essentially of safrole, as is seen from the analyses. They also solidified completely in a freezing mixture, and gave safrole α-nitrosite (m. p. 130°).

Fraction No. 4, b. p. 243—248°. D^{15} 1·039.

0·1435 gave 0·3850 CO_2 and 0·0805 H_2O. C=73·2; H=6·23.
0·2985 ,, 0·1185 AgI. OMe=5·23.

Fraction No. 5, b. p. 248—253°. D^{15} 1·1048.

0·1460 gave 0·3835 CO_2 and 0·0835 H_2O. C=71·6; H=6·36.
0·3920 ,, 0·2200 AgI. OMe=7·40.

Fraction No. 6, b. p. 253—258°. D^{15} 1·1053.

0·1860 gave 0·4895 CO_2 and 0·1080 H_2O. C=71·77; H=6·45.
0·2890 ,, 0·2295 AgI. OMe=10·45.

Fraction No. 7, b. p. 132—137°/12 mm. D^{15} 1·1058.

0·1450 gave 0·3830 CO_2 and 0·0815 H_2O. C=72·04; H=6·25.
0·3150 ,, 0·2203 AgI. OMe=9·23.

Fraction No. 8, b. p. 137—142°/12 mm. D^{15} 1·070.

0·1800 gave 0·4645 CO_2 and 0·1060 H_2O. C=70·38; H=6·54.
0·2890 ,, 0·2945 AgI. OMe=13·44.

Fraction No. 9, b. p. 142—147°/12 mm. D^{15} 1·079.

0·2180 gave 0·5610 CO_2 and 0·1310 H_2O. C=70·19; H=6·68.
0·2635 ,, 0·3595 AgI. OMe=17·90.

Fraction No. 10, b. p. 147—152°/12 mm. D^{15} 1·1087.

0·1555 gave 0·3960 CO_2 and 0·0937 H_2O. C=69·45; H=6·69.
0·2420 ,, 0·4680 AgI. OMe=25·51.

Fraction No. 11, b. p. 152—157°/12 mm. D^{15} 1·1079.

0·1825 gave 0·4610 CO_2 and 0·1140 H_2O. C=68·89; H=6·94.
0·2445 ,, 0·5628 AgI. OMe=30·36.

Fraction No. 12, b. p. 157—162°/12 mm. D^{15} 1·1037.

0·1710 gave 0·4250 CO_2 and 0·1076 H_2O. C=67·78; H=6·99.
0·2705 ,, 0·6585 AgI. OMe=32·11.

Fraction No. 13, b. p. 162—172°/12 mm.

0·1730 gave 0·4380 CO_2 and 0·1158 H_2O. C=69·04; H=7·44.
0·1765 ,, 0·4285 AgI. OMe=32·02.

Residue.—This consisted of a small quantity of dark brown oil, from which plate-like crystals (m. p. 62·5°; palmitic acid) separated on keeping.

On reviewing these results, there is seen to be a definite gradation with rising boiling point of the different fractions, the methoxyl value and the specific gravity increasing whilst the proportion of carbon decreases. This seemed to indicate that the oil consisted mainly of two substances, that of higher boiling point containing methoxyl groups. On closer examination, however, it was found that the latter was not a single substance, but consisted of a mixture of at least two compounds, so similar in character and in boiling point that their separation by physical methods was not practicable.

Action of Bromine on the Portion of High Boiling Point.

Production of Dibromomyristicin Dibromide.

A small quantity of the oil (4 c.c.) from fraction No. 11 was dissolved in light petroleum, and bromine, also dissolved in petroleum, was added drop by drop until in slight excess. During the addition the solution acquired a deep violet tint, but this largely disappeared towards the end of the reaction. A heavy, oily layer separated on keeping, from which a colourless, crystalline solid was deposited. By recrystallisation from methyl alcohol, this substance was obtained in glistening needles, melting at 128·9°. (Found, Br = 62·22. $C_{11}H_{10}O_3Br_4$ requires Br = 62·7 per cent.)

The melting point of dibromomyristicin dibromide is given by Thoms as 130° (*Ber.*, 1903, **36**, 3449), and by Power and Salway as 128—129° (Trans., 1907, **91**, 2055). The identity of the bromo-compound obtained above was proved by its conversion into dibromomyristicin.

A small quantity (1·2 grams) was dissolved in glacial acetic acid (20 grams), and to the solution zinc dust (0·9 gram) was added. The mixture was shaken for a week at the ordinary temperature in a closed flask. The contents were then filtered and the soluble portion diluted largely with water, which dissolved most of the acetic acid. The residual liquor was then extracted with ether, and the ethereal solution evaporated. A viscid liquid with a creosote-like odour remained, which, after a few days, solidified to a crystalline mass. On recrystallising from methyl alcohol, this substance was obtained in needle-shaped crystals, melting sharply at 52°, the melting point of dibromomyristicin (Richter, *Arbeit. Pharm. Inst., Berlin*, 1908, **5**, 167). (Found, Br = 45·4. $C_{11}H_{10}O_3Br_2$ requires Br = 45·4 per cent.)

The formation of these two compounds and the fact that myristicinaldehyde and myristicinic acid are formed on oxidation of this fraction of the oil (see p. 1441) afford definite proof of the presence of myristicin.

Myristicin, however, contains only one methoxyl group, whilst the analyses and the methoxyl determinations of all the high boiling fractions of the oil indicated an average content of two methoxyl groups. It was thus evident that, assuming myristicin to constitute approximately 50 per cent. of this portion of the oil, there must be another constituent present, which contains three methoxyl groups.

This must be a substance of lower specific gravity than myristicin, and in order to explain the analytical results it would require a formula $C_{12}H_{16}O_3$ or thereabouts.

After the removal of the solid dibromomyristicin dibromide from the liquid obtained on bromination, a syrup remained, which did not crystallise:

0·5145 gave 0·6256 AgBr. Br = 57·7.

$C_{11}H_{12}O_3Br_4$ requires Br = 62·7 per cent.

$C_{12}H_{16}O_3Br_2$ „ Br = 43·5 „

This probably consisted of a mixture of a trimethoxydibromo-compound, together with some dibromomyristicin dibromide.

Many attempts were made to separate the trimethoxyl compound in a state of purity, but without success. From the observations already made it was considered to belong to the class of substituted allylbenzene compounds which includes safrole, eugenol, chavicol, myristicin, asarone, etc. The compounds of this group fall into two divisions, according as the ethylenic linking of the side-chain is in the $\alpha\beta$-position (propenyl) or the $\beta\gamma$-position (allyl) with regard to the benzene nucleus. The former are designated *iso*-compounds, and are characterised by their instability when boiled with formic acid, which causes their condensation into complex molecules. The allyl compounds are stable in the presence of formic acid, but can easily be converted into the propenyl isomerides by boiling with alcohol potassium hydroxide.

Myristicin being an allyl compound, the following experiment was made in order to discover whether in the portions of the oil of high boiling point there were present substances containing the propenyl group.

Action of Formic Acid on the Portion of High Boiling Point.—About 6 grams of oil from fraction b. p. 152—157°/12 mm. was heated with pure formic acid on the water-bath for half an hour under reflux. The solution which had become dark purple was poured into water. After the removal of the formic acid, the product was redistilled, and was found to boil almost completely between 273° and 276°, very little condensation having apparently taken place. It was therefore concluded that the constituents of this fraction are allyl derivatives.

Conversion of Allyl Group into the Propenyl Group.—For the purposes of oxidation and obtaining suitable bromo-compounds it was necessary to alter the position of the double linking in the side-chain. This was accomplished by heating the oil (30 grams, fraction 152—157°/12 mm.), together with alcoholic potassium hydroxide (24 grams KOH in 100 c.c. alcohol) (compare Salway, Trans., 1909, **95**, 1208), on the water-bath for twenty-four hours. The alcoholic alkali was afterwards removed by washing, and the oil after extraction with ether, etc., was redistilled.

The myristicin was thus converted into *iso*myristicin, and the other constituents into propenyl derivatives also.

Oxidation of the Mixture of iso-*Compounds. Production of Myristicinaldehyde, Myristicinic Acid, and Trimethylgallic Acid.*—For this purpose 15 grams of the liquid obtained as above were shaken with water, and a solution containing 30 grams of potassium permanganate in 900 c.c. of water was gradually added. The mixture was shaken constantly, and afterwards the flask was heated on the water-bath for a short time. The hot liquid was then filtered from the manganese dioxide and allowed to cool, when it deposited a quantity of colourless, crystalline material.

This melted at 130°, and consisted of almost pure myristicinaldehyde, $C_9H_8O_4$. (Found, C=59·8; H=4·5. Calc., C=60·0; H=4·4 per cent.)

After collecting the crystalline material the aqueous liquid was extracted with ether to remove any aldehyde remaining in solution, and subsequently acidified with hydrochloric acid, when a copious, white precipitate was formed. The acids thus liberated were extracted with ether, and on evaporation of the solution and recrystallisation from hot water were obtained as a crystalline mass melting indefinitely at about 155°. This product was obviously a mixture of acids, and a separation of the constituents was effected by taking advantage of the different solubilities of their calcium salts in water. The mixed acids were dissolved in the smallest possible quantity of ammonium hydroxide solution, and an aqueous solution of calcium chloride was added. After a short time a precipitate separated, but the greater portion remained in the form of a soluble calcium salt.

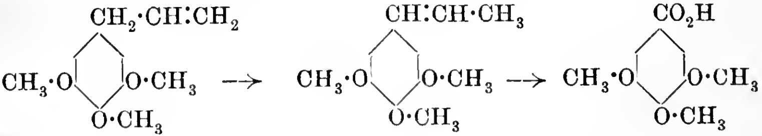
The insoluble calcium salt was suspended in water, acidified with hydrochloric acid, and the mixture shaken with ether to dissolve the liberated acid. On evaporation of the ethereal solution a solid, crystalline acid was obtained, which, after recrystallisation from hot water, was obtained in long needles melting at 212·3°, and was identified as myristicinic acid, $C_9H_8O_5$. (Found, C=55·5; H=4·3. Calc., C=55·1; H=4·1 per cent.)

The aqueous solution containing the soluble calcium salts was acidified with hydrochloric acid, when a copious precipitate separated. This was collected, washed with cold water, and recrystallised from hot water, in which it is fairly readily soluble. It crystallised in long, prismatic needles, melting at 167—168°, and was identified as trimethylgallic acid (3:4:5-trimethoxybenzoic acid), the acid which is obtained on oxidation of *iso*elemicin. (Found, C=56·8; H=5·63; OMe=40·8. Calc., C=56·6; H=5·66; OMe=43·4 per cent.)

The identity of the acid was further confirmed by the production of its methyl ester. This was prepared by passing dry hydrogen chloride into a solution of the acid in methyl alcohol for fifteen minutes, and allowing to remain overnight. The solution was poured into water, neutralised with sodium carbonate, and extracted with ether. On evaporating off the ether a crystalline residue was left, which on recrystallisation from alcohol largely diluted with water, was obtained in long, colourless prisms, melting at 83°.

The methyl ester had previously been obtained by Will (*Ber.*, 1888, **21**, 2022) and by Semmler (*Ber.*, 1908, **41**, 1772) by the methylation of the methyl ester of gallic acid.

The occurrence of trimethylgallic acid (III) in the oxidation products is evidence of the presence of *iso*elemicin (II) in the oil, after treatment with alcoholic potassium hydroxide, and since the behaviour with formic acid indicated the absence of this isomeride in the original oil, it must be there as elemicin (I):



(I.) (II.) (III.)

Unfortunately elemicin does not form a crystalline bromine derivative. *iso*Elemicin, however, forms a solid dibromide, and for the purpose of characterisation this was prepared according to Semmler's method (*Ber.*, 1908, **41**, 2186).

It was obtained in short, colourless prisms, melting at 88—89°.

The greater portion of the bromination products consisted of a mixture of *iso*elemicin dibromide and *iso*myristicin dibromide, which remained as a viscid, semi-solid oil, from which the constituents could not be easily separated.

Conclusion.

The results which have been obtained show that the oil consists in the main of safrole, myristicin, and elemicin. The fractions of the distillate of lower boiling point consist almost entirely of safrole, whilst the intermediate fractions probably contain all three constituents. Fraction b. p. 248—253°, for example, gave safrole nitrosite, and also yielded dibromomyristicin dibromide; the portions of higher boiling point consist principally of myristicin and elemicin.

Besides these, however, there are small quantities of other substances present. These include palmitic acid (m. p. 62·5°), which is present in the free condition, a phenolic substance, and a mixture of the lower fatty acids in the form of esters.

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CLIV.—*The Continuous Fractional Distillation of Water.*

By William Robert Bousfield, M.A., K.C.

In accurate work on the conductivities of dilute aqueous solutions it is recognised that the water employed should approximately have a conductivity which is represented by $\kappa_{18}=1\times10^{-6}$ (which for the purposes of this paper I will take as unit conductivity water). In a former paper (Trans., 1905, **87**, 740) I described an apparatus by means of which water of this order of purity could be produced by continuous fractional distillation from "tap water," that is to say, the ordinary town-water supply. The present paper deals with two forms of apparatus, constructed on the same principles, but of a different and simpler type, and more easily managed. The first of these presents great advantages as a still for everyday use, yielding about 30 litres of water a day (working day and night), two-thirds of which has a conductivity of about 0·8, the remainder being distilled water of ordinary character. The foregoing result is produced without the use of chemicals. If a strong alkaline solution of potassium permanganate is supplied with the feed-water at the rate of about ten drops a minute, water of a slightly lower conductivity may be continuously produced. The other apparatus, which may be referred to as the "three-bottle apparatus," is suited for the continuous redistillation of water under diminished pressure. By the use of this apparatus, water having a conductivity of 0·5 may be continuously produced by the redistillation of the ordinary product of the first still.

The principles on which continuous fractional distillation depends are well known, and would hardly require mention but for the fact that their utility in relation to the distillation of water has been challenged. In ordinary fractional distillation, where the liquid to be distilled contains, let us say, three volatile constituents of different boiling points and the distillate is divided into three fractions, the first fraction usually contains most of the more volatile constituents, the last fraction much of the least volatile constituents, whilst the middle fraction is partly freed from both. In continuous fractional distillation, if the liquid is continuously run into the still and surfaces of different temperatures are simultaneously or consecutively presented for the condensation of the vapours, a steady regime is finally established, and it will be found that the distillate from the hot surface contains little of the most volatile constituent and a larger proportion of the least volatile constituent, whilst that from the coldest surface contains most of the most volatile constituent and little of the least volatile.

In the still described in my former paper, the steam was led into a copper box, in which depended four internally cooled tubes of diverse temperatures. For experimental purposes this was a convenient arrangement, as the products from the tubes differed slightly, and could be separately studied. The hot surface of the copper box and the hottest tube yielded an ordinary distilled water. The cold-surface products from the other three tubes were usually collected together. Their conductivity varied from 1·1 to 1·3; thus the results depended broadly on the continuous separation of the vapour into two products—a hot-surface product and a cold-surface product.

Subsequently Hartley, Campbell, and Poole (Trans., 1908, **93**, 428) employed a modified form of my condenser, in which by a redistillation of distilled water they obtained water of a conductivity of 0·75. In comparing their results with my former and present results, it must be remembered that they did not start with "tap water," and that their fractionation was discontinuous, and the middle fraction only (about 2 litres) reached the desired purity. They employed the hot and cold surfaces, but apparently did not recognise the extent to which these contributed to the result. In discussing my former results they remarked that "the presence of hot and cold tubes was thought to be necessary for the success of the operation," and they concluded that rapidity of condensation was the main factor in the fractionation. It is quite true that the hot surfaces need not be in the form of tubes, but the presence of a sufficient area of hot surface at a sufficiently high temperature was certainly essential. Moreover, I think the hot and cold surfaces were also essential to the result produced in the apparatus of Hartley, Campbell, and Poole, and if they had examined the conductivity of the water from the hot surface of their own still, they would have found that they obtained the same division into hot-and cold-surface products as I did. They were, however, only concerned with the discontinuous fractionation of the cold-surface product.

The recognition of the rôle which the hot and cold surfaces play is so vital that I may be excused for describing two simple experiments which illustrate it. For the purpose of these experiments I used the three-bottle still described later on, in which the air of the laboratory can play no part. The second bottle, *B* (see Fig. 3), served as the hot surface, being swathed in cloth and cotton-wool, and the collecting bottle, *C*, over which a stream of cold water flowed, served as the cold surface.

Experiment I.—To 8 litres of good distilled water having a conductivity of 1·5 were added 8 drops of acetic acid, which raised the conductivity to 20. This water was introduced into bottle *A*, and distilled under diminished pressure at a temperature of about 35°. Four litres condensed in bottle *C*, whilst half a litre condensed in bottle *B*. The resulting conductivities were:

Hot-surface product (bottle *B*)	24
Cold-surface product (bottle *C*)..............	12

Experiment II.—To 8 litres of distilled water having a conductivity of 1·5 were added 8 drops of strong ammonia solution, which raised the conductivity to 24. The water was distilled under the same conditions as before, giving similar volumes of distillate in the two bottles. The resulting conductivities were:

Hot-surface product (bottle *B*)	2·5
Cold-surface product (bottle *C*)	35·0
Residue undistilled	6·0

These two experiments illustrate clearly the rôle which the hot and cold surfaces play in relation to volatile impurities of higher and lower boiling point than water. They also show that the predominating impurities determine whether the hot-surface product or the cold-surface product will be the better.

In applying these principles to the purification of water we have to reckon with a complex volatile organic constituent which appears to have a higher boiling point than water, but which is partly decomposed by prolonged boiling, giving rise to products, one of which, namely, ammonia, is very volatile. How the impurities will be distributed on fractionation depends partly on the amount of boiling, as well as on the temperatures of the condensing surfaces. Redistillation of distilled water without fractionation often gives a product containing more free ammonia than the original water, but small variations of the conditions of distillation sometimes give abnormal results. In the following illustrations the water to be redistilled was boiled in a Jena-glass flask of about

3½ litres capacity. The vapour was condensed in a silver condenser without fractionation. About 2 to 2½ litres were placed in the flask, and it all passed over except about 5 c.c. at the beginning and 40 c.c. at the end. The relative ammonia contents as indicated by a comparison of colours after the addition of equal quantities of Nessler's reagent are given in arbitrary units merely for the sake of comparison. The quantity of ammonia did not in any case exceed 3 parts in 10^8. The distillation was conducted at the same rate in each experiment.

Redistillation of Distilled Water.

	Before redistillation.		After redistillation.	
No.	Conductivity.	Ammonia.	Conductivity.	Ammonia.
1	5·0	3	0·9	2
2	0·9	2	0·9	3
3	2·2	2	0·9	3

In the first experiment there was a reduction of free ammonia contents, perhaps due to a higher temperature of condensation. In the second experiment the water taken was the product of the first experiment. Its conductivity was unchanged by the second redistillation, but the free ammonia content increased 50 per cent. In the third experiment the conductivity was reduced to less than half, but again the free ammonia content was increased. The second and third experiments are typical of what usually occurs. From these examples it is clear that when we are fractionally distilling water by the use of hot and cold surfaces it may be found that under one set of conditions the hot-surface product is the purer, as tested by its conductivity, and under another set of conditions the cold-surface product. For practical purposes it is sufficient to fractionate the distillate into two products, one continuously deposited on a hot surface and the other on a cold surface.

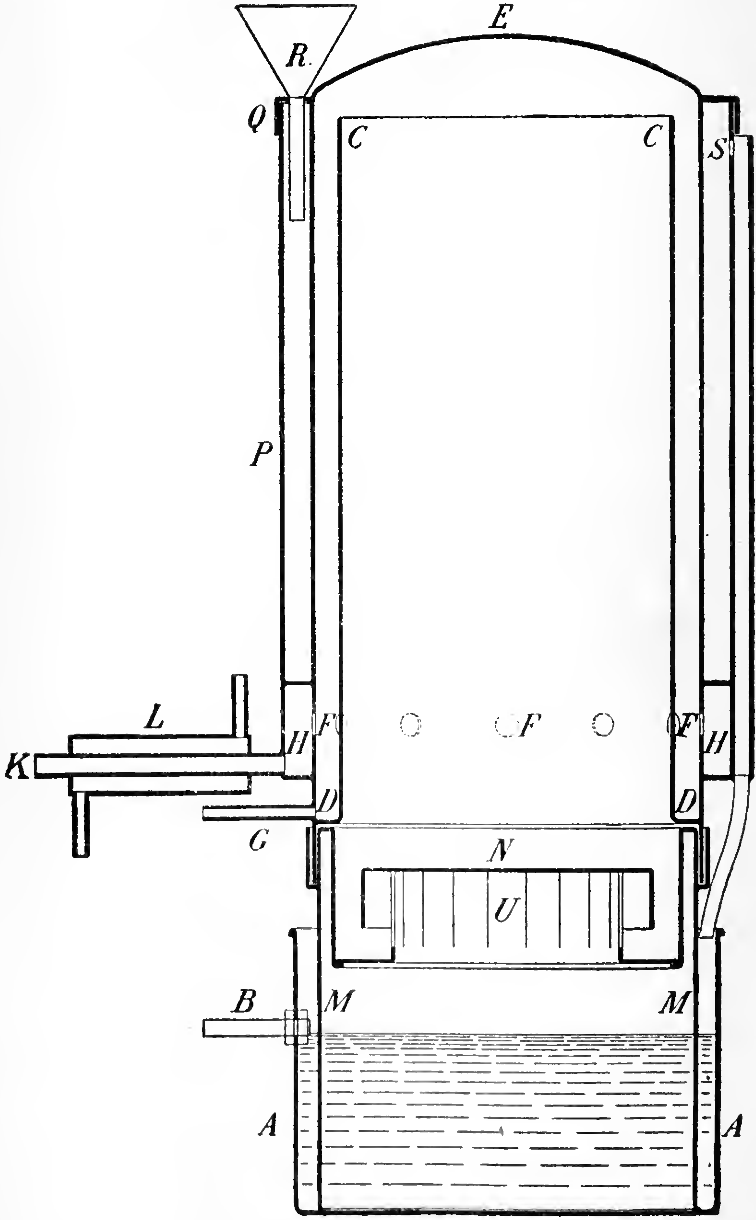
In the still described in my former paper, the conditions were such that the cold-surface product was the purer. This appears also to have been the case with the still of Hartley, Campbell, and Poole, although they do not actually give the conductivity of their hot-surface product. In the first of the two stills which I am about to describe, the hot-surface product is the purer. This is probably due to the prolonged boiling having the effect of decomposing a large part of the complex organic compound, so that ammonia is the chief impurity to be dealt with. In the second of the two stills hereinafter described, as in my original still, the cold-surface product is the purer. This product is, I believe, purer than that hitherto produced on a large scale by any previous arrangement of still. It seems probable that further redistillations with hot- and cold-surface fractionation might give results approximating to the unique result produced by Kohlrausch on a small scale (*Ann. Phys. Chem.*, 1894, [iii], **53**, 209). The present paper, however, deals only with the practical problem of producing "conductivity water." Water of a higher degree of purity than is correlated by a conductivity of 0·5 is very difficult to preserve.

Description of New Still and Condenser (Fig. 1).—The water to be distilled is boiled in an open pan, *A*, furnished with an overflow pipe, *B*, at the side. The main condenser consists of a double cylinder of block tin ending above in a dome, which is shown in section by the lines *C*, *D*, *E*. These cylinders form a pocket, *D*, at their lower end, in which water condenses, and from which it is led away by the pipe *G*. This is furnished with a bent glass tube (not shown), which enters the neck of the collecting bottle. Round the outer surface of the main condenser, at a short distance above the pocket, there is provided a series of holes, *F*, through which the vapour which is not condensed in the pocket passes into an annular chamber, *H*. This is connected at one side to an escape pipe, *K*, which serves as an auxiliary condenser, being surrounded with a water circulation jacket, *L*. The main condenser is for convenience of manufacture jointed by means of a water-sealed joint to a copper cylinder, *M*, which is open at the bottom, and stands in the open pan, *A*. The spray arrester, *N*, consists of a short cylinder furnished with suitable slits, *U*, through which the steam issues tangentially, and within a cap, *N*, which deflects the steam downwards. The cyclonic action set up by the tangential flow causes spray to be deposited and to run back into the pan. The main condenser is jacketted by an outer cylinder, *P*, which is covered with a loose lid, *Q*, in order to arrest the escape of steam. Condensing water is supplied by a funnel, *R*. The quantity required is very small, and it escapes by an overflow, *S*, and is delivered by a pipe, *T*, as feed-water into the pan, *A*.

In operation the flow of condensing water into the funnel, *R*, is so regulated that the temperature of the main condenser varies from 100° at the top to about 95° at the bottom. Under these conditions, if the water in the pan is vigorously boiled with a suitable ring-burner supplied with gas at 2 inches water-pressure, about two-thirds of the vapour is condensed in the main condenser. The surplus one-third passes through the holes *F* into the annular ring *H*, and is condensed at *K*.

The flow of gas and water require careful adjustment, which is soon learned by experience. If, for instance, with full gas supply, excess of condensing water is supplied through *R* so that the temperature at the bottom of the main condenser falls below 90°, the

Fig. 1.



whole of the vapour will be condensed in the main condenser, and there will be little or no fractionation. If, on the other hand, too little condensing water is supplied, there will be little condensation in the main condenser, and the bulk of the water will be condensed in *K*. With a steady gas-pressure and water-pressure, however, the still may be left to itself through the night without any interference.

The arrangement of open pan with open-bottomed cylinder standing in it is extremely convenient, as it enables the apparatus to be readily cleansed from scale or other deposit which collects in the pan. But the part which the open pan plays in purification is more essential. Feed-water is supplied in the open annulus between the pan and the cylinder. It has gradually to make its way downwards until it passes underneath the bottom of the open cylinder into the interior. During this passage from the exterior to the interior, the organic impurity of higher boiling point is largely decomposed before the liquid reaches the interior of the cylinder, so that the ammonia thus liberated, and also the carbon dioxide and dissolved air contained in the water, are boiled off and escape into the open air instead of passing through the still. I regard this feature as materially contributing to the improved results which this still gives.

Owing, as I believe, to the prolonged boiling of the water in the outside of the pan, the impurity of high boiling point gives much less trouble. In my former still the cold-surface product was the purer product, and the hot-surface product was rejected. In this still, on the contrary, the hot-surface product is the purer product. I ought to mention that my laboratory was at the time of my former experiments supplied with West Middlesex water, and is now, as I am informed, supplied with New River water; but I do not attribute any importance to this. The hot-surface product now obtained is a good deal better than the former cold-surface product. I am now able to obtain continuously from "tap water," in one distillation without the use of chemicals, water of a conductivity 0·8. Part of the improvement is due to the new spray arrester. If this is removed the water produced has a conductivity of 0·9 instead of 0·8.

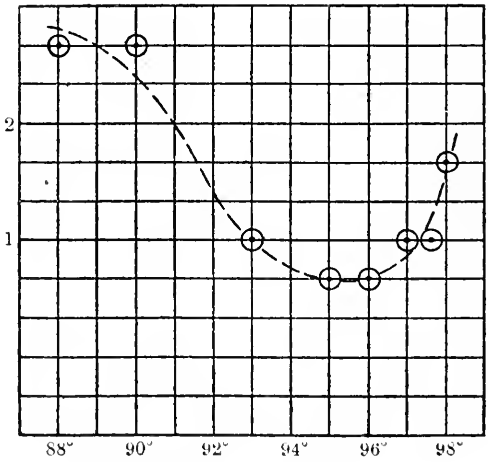
In the following table and in Fig. 2 are shown the results of varying the temperature of the main condenser by varying the flow of condensing water. The first column gives in c.c. the quantity of the cold-surface distillate for 1 litre of hot-surface distillate. The second column gives the flow of condensing water into the outer jacket of the main condenser in c.c. per minute. The third column gives the temperature of the condensing water in the outer jacket near the bottom. At the top it would always be nearly 100°. The two last columns give the conductivities of the hot- and cold-surface products.

Table of Results of Distillation with Varying Condenser Temperatures.

Quantity of cold product in c.c.	Condensing water per minute in c.c.	Condenser bottom temp.	κ_{18}	
			Hot product.	Cold product.
1200	20	98·0	1·4	8
1000	30	97·5	1·0	5
1000	50	97·0	1·0	5
700	70	96·0	0·8	5
500	100	95·0	0·8	7
100	120	93·0	1·0	8
0	130	90·0	2·0	
0	150	88·0	2·0	

It should be observed that as in this case we are taking the hot-surface product, it is immaterial what is the temperature of the auxiliary condenser. The product of the auxiliary condenser is very variable, depending on the flow of condensing water through it. If it is kept hot some of the steam may escape uncondensed, but this does not affect the main product, and regulation of the temperature of the auxiliary condenser is unnecessary. It will be observed that the purest water is obtained from the hot surface when the proportions of distillate collected from the hot and cold

FIG. 2.



x = temperature. $y = \kappa_{18} \times 10^6$.

surfaces are about two to one. The rate of total distillation in all the cases given in the table is approximately the same, namely, about 1⅓ litres per hour, produced by the use of 2 inches gas-pressure in the burner. The minimum in the curve shown in Fig. 2 is produced by two causes. To the left we have lower mean temperatures of condensation, which allows more ammonia to condense with the water. To the right of the minimum, the higher temperature of the condensing surface diminishes the water-flow over the large tin surface to such an extent that the proportion of any soluble matter which might be taken up from the tin surface is increased. It is surprising that such good water can be distilled from a hot tin surface, considering the very large area of contact between the hot tin surface and the water.

No special care was taken in the collection of the water in any of the experiments with this still. The water runs from the condenser through a bent hard-glass tube into an open 3-litre Jena-glass flask with the usual long neck. As the water drips into the flask at a temperature of from 80° to 90°, there is a constant slight escape of vapour from the neck of the flask, which may serve to some extent to prevent contamination by the air of the laboratory.

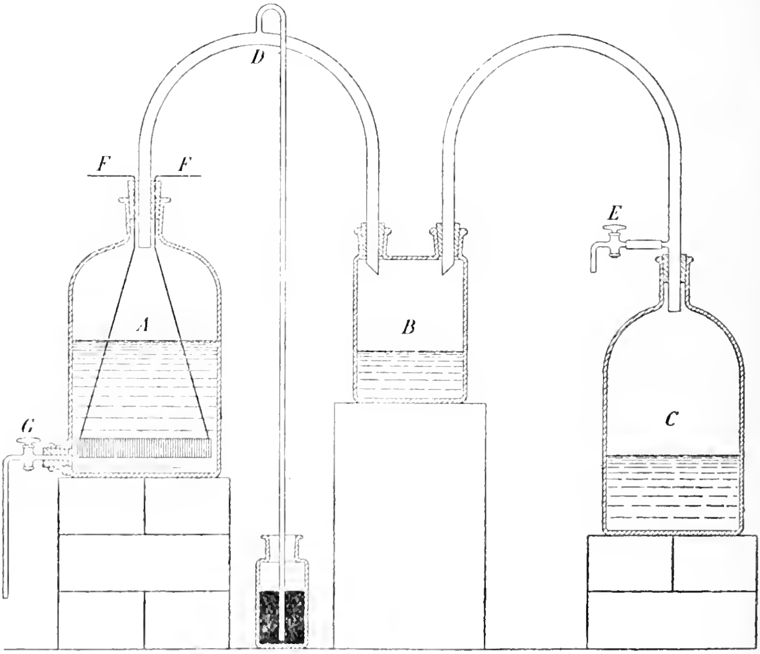
The addition of a strong alkaline solution of potassium permanganate to the water in the outer annulus of the pan at the rate of about 10 drops per minute produced only a slight further purification, reducing the conductivity of the water produced to 0·75. In this particular experiment very vigorous boiling took place, produced by a gas-pressure of 3 inches. Probably somewhat better results could have been obtained with slower boiling, as the normal best product without the use of chemicals has a conductivity of only 0·9 with 3 inches gas-pressure, as against a normal product of conductivity 0·8 with 2 inches gas-pressure.

A curious result appeared when a considerable excess of the alkaline permanganate was used, which is noted below. In each of the three cases set out the still was regulated so as to give approximately 2 litres of distillate from the hot surface for 1 litre from the cold surface, the rate of distillation being such as to give a total output of about 1½ litres per hour with 3 inches gas-pressure.

	κ_{18}.	
	Hot-surface product.	Cold-surface product.
1. From tap water only	0·9	10·0
2. With a large addition of alkaline permanganate	1·2	2·0
3. With ten drops per minute	0·75	2·8

Three-bottle Still.—For the further purification of distilled water I have found the three-bottle still shown in Fig. 3 to give the best results. It consists of three bottles, *A*, *B*, and *C*, connected by bent tubes of hard glass and rubber corks. *A* is an ordinary aspirator bottle of about 8 litres capacity, furnished with a stopcock and tube, *G*, of about 1 mm. bore. It is filled about two-thirds full with the water to be distilled, and replenished from time to time by sucking in water through this tube. *B* is an ordinary two-necked bottle of about 2 litres capacity. *C* is an 8-litre bottle of green-coloured glass of the kind in which I usually store water. An electric heater in bottle *A* is the source of heat. The operation is carried on under diminished pressure. A by-pass tube, *D*, serves for connexion to a barometer tube for indicating the pressure, and a by-pass, *E*, is connected through a tap to a good filter-pump. The electric heater is immersed in the water, and consists of about 270 ohms of enamelled nickel-chrome wire, wound on a strip of mica. The leads, *F F*, which are connected to the power mains with a pressure of 240 volts alternating current, consist of silver wire of 1 mm. diameter. They were passed through the rubber cork by first making perforations with a stout pin. The holes were caulked with rubber solution. The enamel of the heating wire was not a very good insulator, and set up some electrolysis of the water,

Fig. 3.



to prevent which the leading-in wires immersed in the solution were surrounded by glass tubes. In this arrangement a small quantity of potassium hydrogen sulphate (2 or 3 drops of a strong solution to each litre of water) was used in order to retain ammonia. The cold-surface product in bottle *C* is now the purest. Bottle *B* was swathed in cotton-wool in order to maintain it at a temperature of only two or three degrees below that of *A*, and it should be noted that the first half of each of the bent connecting tubes was also wrapped in cotton-wool. A stream of cold water was caused to flow over bottle *C*. This was distributed over the surface by winding a few turns of thick string spirally round the bottle. The redistillation in this apparatus of the product of the first still at a temperature of about 40° gives water of a conductivity of 0·5. The small quantity condensed in bottle *B* usually has a conductivity about two or three times as great as that in *C*.

No spray trap was found to be necessary. The form of the bent connecting tubes and the delivery of the vapour vertically downwards into the hot-surface bottle *B*, sufficed to eliminate spray from the final product. The water from this apparatus (conductivity 0·5) is the purest I have hitherto been able to produce in large quantities by continuous fractionation.

Probably this high degree of purity is due partly to the fact of the two successive distillations, in the first of which the hot-surface product is taken, and in the second of which the cold-surface product is taken. Distillation in the first still eliminates most of the free ammonia. Redistillation in the second still eliminates much of the volatile impurity of higher boiling point which has escaped decomposition.

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CLV.—*Pyrogenic Decompositions. Part I. Benzene.*

By CLARENCE SMITH and WILLIAM LEWCOCK.

SOME time ago one of the authors was engaged in examining the pyrogenic decomposition of American turpentine with the object of obtaining isoprene in quantity. The results of the investigation confirm, in the main, those of Tilden (Trans., 1884, **45**, 410), but the research was discontinued because information was received that other workers were obtaining isoprene from turpentine in almost quantitative yield by a similar process. The experiments proved conclusively, however, that the yield of isoprene is affected very greatly by the duration of the heating and the temperature of the tube. Since it appears that by proper adjustment of these two factors the conversion of turpentine into isoprene is almost quantitative, it seems desirable to examine the pyrogenic decomposition of other organic substances, in the hope that by again suitably adjusting the two factors in question the decomposition might take a unique, or almost unique, course. The first substance selected for examination was benzene.

The pyrogenic decomposition of this hydrocarbon in an iron or porcelain tube has been described by various investigators (Berthelot, *Zeitsch. Chem.*, 1866, 707; Schultz, *Annalen*, 1874, **174**, 201; *Ber.*, 1876, **9**, 547; Aronheim, *Ber.*, 1876, **9**, 1898; Smith, *Ber.*, 1879, **12**, 722; Hübner, *Annalen*, 1881, **209**, 339; La Coste and Sorger, *Annalen*, 1885, **230**, 5). Berthelot mentions that the yield of diphenyl is influenced by the rate of flow of the benzene and the temperature at which the decomposition is effected (*Ber.*, 1872, **5**, 682), but the other workers appear not to have appreciated the prime importance of these two factors. The temperature of the tube is described vaguely as "at a bright red heat" or "at an intense heat," whilst the rate of flow of the benzene is often not mentioned. Schultz states that the rate should be 100—200 grams of benzene per hour, and that the tube should not be heated too intensely. Moreover, he alone records his yield of diphenyl, 30—40 per cent., the others merely stating that the yield is "considerable" or "satisfactory."

In our experiments an iron tube has been used, although such an apparatus suffers from a serious objection. The temperature, as measured by a thermometer, of the tube is only the average temperature of the gaseous molecules within the tube; some of the molecules will be at a higher, others at a lower, temperature than the average. Since the course of the decomposition is affected so markedly by temperature, it seems unlikely that the heating of benzene vapour in a length of iron tube can result in a unique decomposition. An apparatus in which this defect is mitigated is under consideration, but the results of the experiments here recorded indicate that even in an iron tube an approach to the decomposition of benzene along a single course is possible.

The tube is placed, sloping downwards, in an ordinary combustion-furnace, and is attached at its upper end to the side-tube of a copper distilling flask. In the neck of the flask is fitted a separating funnel, from which the benzene is allowed to fall, drop by drop, into the flask heated to about 150°. The sound of the falling drops furnishes a ready means of regulating the rate of flow of the benzene. With the object of cooling the products of the decomposition as rapidly as possible, and thus preventing secondary changes, the lower part of the iron tube, just outside the furnace, is provided with an inlet, through which water is run into the lower part of the tube at such a rate that the water issuing, together with the condensed products of the decomposition, from the end of the tube is still cold. The end of the iron tube is attached by lead composition piping to one neck of a three-necked bottle of about 5 litres capacity. A second neck of the bottle is fitted with a siphon tube, whereby the water can be drawn out of the bottle as fast as it runs in from the tube. The third neck is attached by glass tubing to the condensing apparatus. This consists of a pair of vertical 6 ft. iron water condensers, arranged in series, the exit tube of the second condenser being attached to a worm condenser cooled in a freezing mixture. This arrangement is essential when turpentine is being decomposed, but with benzene it is found that the products of the decomposition that can be condensed at ordinary temperatures and pressures collect in the three-necked bottle, very little liquid being found in the condensers. At the conclusion of the experiment the water in the bottle is siphoned off as completely as possible, the liquid decomposition product is collected, dried by calcium chloride, and fractionated. It consists almost entirely of unchanged benzene and diphenyl, the quantity of substance boiling above 260° being extremely small; in fact, only about 10 grams have been obtained from some 7—8 litres of benzene.*

The temperature of the tube is measured by a copper-nickel or platinum-iridium thermo-couple in conjunction with a Paul galvanometer reading to fifths of a millivolt. By adjusting the individual burners of the furnace and regulating the gas pressure, it is possible to heat the iron tube uniformly to within 5—10°. When turpentine is being decomposed, the best yield of isoprene is obtained by passing the terpene very rapidly (250 c.c. in three to four minutes) through the tube; the rapidly-rushing vapour lowers the temperature of the tube by 30—40°, and therefore it is necessary to retain the thermo-couple in the tube during the experiment. In the case of benzene, however, the hydrocarbon is admitted so slowly (5 c.c. per minute) that the temperature of the tube is not appreciably affected, and the thermo-couple need not be in situ during the experiment, a matter of great practical convenience.

The results of the experiments on benzene are recorded in the table.

* The benzene used was Kahlbaum's benzene cryst., free from thiophen.

Pyrogenic Decomposition of Benzene.

Expt.	C.c. benzene.	Time, minutes.	Temperature.	Length and diam. of tube, cm.	Benzene recovered, c.c.	Di-phenyl, gram.	Di-phenyl, per cent.	Remarks.
1	100	20	600	73 1·1	90	—	—	
2	,,	,,	,,	,,	,,	—	—	BaO_2 in tube
3	,,	,,	670	,,	89	2	21	,, ,, ,,
4	,,	,,	685	,,	75	5	23	
5	,,	30	760	,,	58	9	24	
6	85	17	800	36 1·1	40	4	10	
7	100	20	,,	24 1·1	65	7·5	24	
8	,,	19	655	73 3·2	78	5	26	
9	,,	25	,,	,,	,,	,,	,,	Al_2O_3 in tube
10	,,	20	,,	,,	69	,,	18	ZnO in tube
11	,,	7	685	,,	78	4	21	
12	,,	22	,,	,,	63	9	28	
13	,,	20	720	,,	77	6·5	32	
14	,,	,,	,,	55 3·2	80	9·5	54	
15	90	,,	,,	36 3·2	61	11	43	
16	100	25	,,	24 3·2	82	6	38	
17	,,	20	760	36 3·2	78	8·5	44	
18	,,	,,	,,	55 3·2	68	12	43	
19	,,	13	795	24 3·2	73	9	38	
20	,,	20	,,	,,	72	13	53	
21	,,	,,	800	36 3·2	62·5	14	42	
22	,,	,,	680	55 3·2	52	9·5	28	
23	,,	,,	,,	,,	81	6	36	Pb_3O_4 in tube. Reduced by carbon
24	200	42	760	,,	130	36·5	59	BaO_2 in tube.
25	200	30	680	,,	158	14	38	One-half of the recovered benzene was passed again through the tube. 172 c.c.
	86	18	,,	,,	42	5	13	

In experiments 1—7 a rather narrow iron tube was used. At 600° the formation of diphenyl has not been observed. By heating benzene under pressure in an iron tube, Ipatieff has also observed that diphenyl is not produced below 600° (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 681). In experiment 2 a layer of barium peroxide was placed in the tube in the hope that the mobile oxygen atom would exert sufficient attraction for two hydrogen atoms in 2 molecules of benzene to cause the formation of diphenyl. This expectation was not fulfilled at 600°, but it has been at a higher temperature. Experiments 3—5 illustrate the effect of increase of temperature. In experiment 6, one-half of the tube was heated at 800°; the yield of diphenyl, only 10 per cent., shows that the optimum temperature for the formation of diphenyl has been exceeded. Experiment 7, in which one-third of the tube was heated at 800°, shows, however, that the formation of diphenyl is influenced, not only by the temperature, but also by the time the benzene vapour is kept at the temperature.

In the experiments with the narrow iron tube some trouble was experienced owing to the deposition of carbon and consequent choking of the tube. A wider tube, 3·2 cm. in diameter, was tried. Experiment 8 shows that the increased cross-section of the tube is materially beneficial, since at 655° a better yield of diphenyl is obtained than that in the narrow tube at higher temperatures (experiments 3 and 4).

The influence of catalysts in the tube was tested, not hopefully, however, because their surface must rapidly become coated with carbon. Experiments 9 and 10 show that our fears were well founded. Experiments 11 and 12 illustrate again the influence of the duration of the heating on the production of diphenyl, as also do experiments 13—16, although in these the duration of the heating is shortened, not by admitting the benzene more rapidly, but by diminishing the length of the heated portion of the tube. Experiments 17—21 show that the yield of diphenyl is not increased at temperatures higher than 720°, although experiment 20, in comparison with experiment 13, illustrates once again the fact that the effect of a short heating at a higher temperature may be greater than that of more prolonged heating at a lower temperature.

Experiments 22 and 23 having shown that the presence of an easily reducible metallic oxide in the tube leads to an increased yield of diphenyl, the effect of barium peroxide was tried again (experiment 24), at a higher temperature than in experiment 2. The result was a 59 per cent. yield of diphenyl, the best that has been obtained with the apparatus and the water-cooling device employed in the preceding experiments. Evidently, however, the method is of little use in a continuously-working apparatus, because operations must be stopped when the barium peroxide has been reduced to the oxide, in order that the oxide may be replaced by fresh peroxide or reconverted into the peroxide by intense ignition in air or oxygen.

It will be noticed that a very large percentage of the benzene used is recovered unchanged. Sabatier has shown that the addition of hydrogen to ethylene at 200° in the presence of finely-divided metals becomes reversed at 250—300°, ethane decomposing into ethylene and hydrogen. Also, according to Zelinsky, *cyclo*hexane in the presence of palladium decomposes into benzene and hydrogen at 170°, but exists in equilibrium with these two substances at 200°. Possibly, therefore, the conversion of benzene into diphenyl and hydrogen at a high temperature may be a reversible process, the condition of equilibrium being well in the direction of a large concentration of benzene. We have tried to prove the reversibility of the reaction by passing hydrogen and the vapour of diphenyl through our apparatus, but the experimental difficulties are considerable, and we have been unable definitely to identify benzene among the substances issuing from the tube.

Experiment 25 shows that no advantage is gained by passing the condensed product of decomposition through the tube again. The condensed product, 172 c.c., was divided into two equal portions. One portion was fractionated, and gave 79 c.c. of benzene and 7 grams of diphenyl; the other portion was passed again through the tube, and then yielded only 5 grams of diphenyl.

The conditions of experiment 14 have been selected as the most suitable under which to work an apparatus for the continuous conversion of benzene into diphenyl. The apparatus described above is modified by removing the water-cooling device and the condensers. The side inlet of the iron tube is plugged with a mixture of litharge and glycerol, and the end of the tube is connected by a bent iron pipe to the lower end of a vertical iron condenser, 55 cm. in length, enclosed in a steam-jacket. The upper end of the iron condenser is attached to an ordinary Liebig water-condenser, which slopes downwards with its end above a filtering funnel placed in the neck of the separating funnel attached to the copper distilling flask. When the apparatus is in operation, the vapours issuing from the iron tube pass up the steam-jacketted iron condenser in which the diphenyl is condensed, and collects at the bottom; the benzene vapour passes on to the water-condenser and is there liquefied, the liquid benzene ultimately flowing back into the copper distilling flask.

When this apparatus was employed under the conditions of experiment 14, the yield of diphenyl was only 30—40, instead of 54 per cent. Being at a loss to account for the decreased yield, we performed experiments in which the rate of flow of the benzene and the length of the heated tube were varied, and found finally that the conditions of experiment 14 were the best, with the single alteration that the length of the heated tube should be 36 instead of 55 cm. Evidently, when the water-cooling device is being used, as in experiment 14, the end of the iron tube is so cooled by the water entering the side-inlet that the length of the heated portion of the tube, although apparently 55 cm., is in reality less than this. When the water-cooling device is not being used, a shorter length, only 36 cm., of the tube must be heated in order to give the best yield of diphenyl. This discovery furnishes a very striking illustration of the extent to which the formation of diphenyl is affected by a slight change in the experimental conditions.

With the continuously-working apparatus and under the revised conditions of experiment 14, at times the yield of diphenyl reaches 70 per cent. The average yield, however, is about 65 per cent.; for example, in one experiment a litre of benzene was passed through the apparatus; 912 c.c. of benzene were recovered, and 50 grams of diphenyl were drawn off from the steam-jacketted condenser.

Unfortunately, one of us is compelled to retire from the investigation. We considered it desirable, therefore, to publish the results which we have obtained jointly, although the continuously-working apparatus is in some respects not as satisfactory as could be desired; for example, no satisfactory arrangement for drawing off the liquid diphenyl from the condenser has been introduced. In practice this is of not much importance, because it is necessary to stop operations after about 300 c.c. of benzene have been passed through the tube, in order to remove the deposit of carbon in the tube; unless this is done, a marked falling off occurs in the yield of diphenyl. During the stoppage the diphenyl can be run off from the bottom of the condenser.

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CLVI.—*The Influence of Colloids and Fine Suspensions on the Solubility of Gases in Water. Part II. Solubility of Carbon Dioxide and of Hydrogen.*

By ALEXANDER FINDLAY and BUCCHOK SHEN, M.Sc., A.I.C.

IN a paper by Findlay and Creighton (Trans., 1910, **97**, 536) the results of an investigation of the solubility of carbon dioxide and nitrous oxide in water in presence of colloids and fine suspensions were communicated. In view of the results then obtained it was decided to continue the investigation; and for the purpose of ascertaining in how far the behaviour of colloids is a peculiar one, the solubility of carbon dioxide in solutions of ammonium chloride, potassium chloride, barium chloride, ferrous ammonium sulphate, sucrose, and chloral hydrate has been determined at different pressures. Further, the solubility of carbon dioxide in solutions of methyl-orange has been studied in order to compare the solubility curve with that obtained with ferric hydroxide and aniline (Findlay and Creighton, *loc. cit.*); and lastly, the influence of the colloids peptone, propeptone, and hæmoglobin on the solubility of carbon dioxide has been investigated. Hæmoglobin was included among the colloids investigated on account of the behaviour of blood towards carbon dioxide (Findlay and Creighton, *Biochem. J.*, 1911, **5**, 294). In the present communication also are included the results of a series of determinations of the solubility of hydrogen in water in presence of dextrin, starch, gelatin, ferric hydroxide, and suspension of silver.

All determinations were carried out at 25°, the apparatus employed being the same as that used by Findlay and Creighton.

I.—*Solubility of Carbon Dioxide.*

For the following determinations carbon dioxide (0·05 per cent. of impurity), prepared by the action of hydrochloric acid on marble, was employed. This must be borne in mind in comparing the present results with those obtained by Findlay and Creighton, who used commercial carbon dioxide.

TABLE I.

Solubility of Carbon Dioxide in Water.

Pressure (mm. Hg)	759	841	934	1069	1210	1350
Solubility	0·825	0·826	0·824	0·823	0·825	0·826
Pressure	755	836	927	1084	1211	1350
Solubility	0·826	0·825	0·826	0·825	0·825	0·824

These and other determinations which were carried out at regular intervals as a check on the accuracy of subsequent measurements give the value 0·825 for the solubility of carbon dioxide in water, a number which is in excellent agreement with that obtained by other workers.

Solubility of Carbon Dioxide in Solutions of Ammonium Chloride, Potassium Chloride, Barium Chloride, Ferrous Ammonium Sulphate, Sucrose, and Chloral Hydrate.

In the case of these solutions, both of electrolytes and of non-electrolytes, the solubility of carbon dioxide was less than in water;

and the more so the greater the concentration of the solution. Since, in all cases, the solubility was independent of the pressure, it suffices to give the mean values of solubility obtained. By concentration is meant, in the following tables, the number of grams of solute in 100 c.c. of solution. In the case of barium chloride and ferrous ammonium sulphate, the number refers to the hydrated salt.

(*a*) *Ammonium Chloride:*

Concentration.	Density.	Solubility of CO_2.
2·35	1·005	0·791
5·05	1·013	0·754
8·24	1·022	0·732
10·02	1·027	0·712
17·09	1·045	0·665

(*b*) *Potassium Chloride:*

Concentration.	Density.	Solubility of CO_2.
1·84	1·008	0·792
3·05	1·017	0·764
4·58	1·026	0·749
7·46	1·044	0·701

(*c*) *Barium Chloride:*

Concentration.	Density.	Solubility of CO_2.
2·80	1·018	0·789
5·81	1·040	0·741
8·15	1·054	0·710
9·97	1·070	0·676

(*d*) *Ferrous Ammonium Sulphate:*

Concentration.	Density.	Solubility of CO_2.
9·51	1·052	0·641
10·26	1·057	0·629
22·47	1·124	0·460

(*e*) *Sucrose:*

Concentration.	Density.	Solubility of CO_2.
2·63	1·009	0·813
5·16	1·018	0·798
9·68	1·038	0·767
12·33	1·051	0·744

(*f*) *Chloral Hydrate:*

Concentration.	Density.	Solubility of CO_2.
5·08	1·019	0·815
10·12	1·041	0·795

Solubility of Carbon Dioxide in Solutions of Methyl-orange.

TABLE II.

Concentration, 0·309. Density, 0·998.

Pressure......	726	823	915	1056	1191	1319
Solubility ...	0·831	0·833	0·829	0·827	0·826	0·826

Concentration, 0·428. Density, 1·000.

Pressure......	738	838	932	1075	1215	1344
Solubility ...	0·855	0·850	0·844	0·838	0·835	0·831

Concentration, 0·593. Density, 1·002.

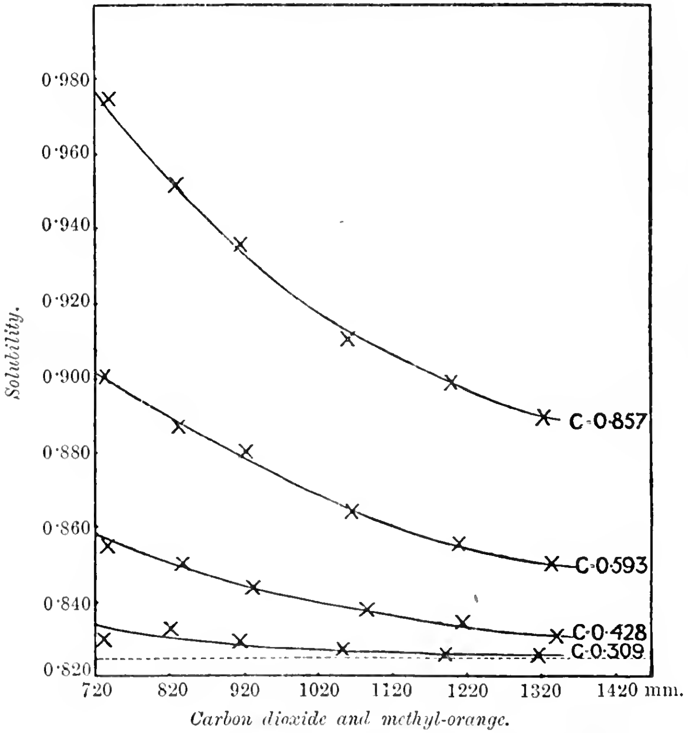
Pressure......	732	832	924	1068	1209	1335
Solubility ...	0·900	0·887	0·880	0·864	0·855	0·850

Concentration, 0·857. Density, 1·004.

Pressure......	729	829	918	1063	1203	1326
Solubility ...	0·975	0·952	0·936	0·915	0·899	0·890

These results are represented graphically in the diagram: the dotted line represents the solubility of carbon dioxide in water.

Solubility of carbon dioxide in solutions of methyl-orange.



Solubility of Carbon Dioxide in Solutions of Peptone, Propeptone, and Haemoglobin.

(*a*) *Peptone.*

Commercial peptone was employed, and was only partly soluble in water. The solution was decanted from the insoluble portion.

TABLE III.

Concentration, 0·81. Density, 0·999.

Pressure......	754	855	947	1092	1238	1357
Solubility ...	0·863	0·857	0·855	0·852	0·848	0·846

Concentration, 1·68. Density, 1·002.

Pressure......	750	852	962	1092	1230	1353
Solubility ...	0·893	0·884	0·875	0·870	0·862	0·859

Concentration, 3·07. Density, 1·007.

Pressure......	750	851	945	1089	1234	1354
Solubility ...	0·932	0·923	0·913	0·901	0·891	0·885

The solubility curve is similar to that for methyl-orange.

In these solutions absorption of gas took place very rapidly, and was accompanied, on approaching the point of saturation, by froth formation.

(*b*) *Propeptone.*

The propeptone used in these experiments was prepared as follows (E. Salkowski, *Jahresber. über die Fortschritte der Tierchemie*, 1880, 26; compare Pekelharing, *ibid.*, 1880, 28). Fifty grams of commercial peptone were dissolved in warm water, the solution being decanted from the insoluble portion. After being boiled in presence of acetic acid, the cooled solution was saturated with sodium chloride, filtered, and the precipitate washed with dilute salt solution. The precipitate was redissolved in 300 c.c. of warm water, and reprecipitated by salt and a little acetic acid. A solution of the propeptone so obtained was then dialysed until free from chloride.

TABLE IV.

Concentration, 0·299. Density, 0·998.

Pressure......	751	851	947	1092	1233	1358
Solubility ...	0·838	0·838	0·835	0·832	0·831	0·831

Concentration, 0·802. Density, 1·000.

Pressure......	743	842	935	1079	1219	1347
Solubility ...	0·851	0·848	0·845	0·841	0·840	0·839

These results yield a solubility curve of the same form as that obtained with methyl-orange.

(c) *Haemoglobin.*

Commercial hæmoglobin was employed.

TABLE V.

Concentration, 0·199. Density, 0·998.

Pressure......	732	830	923	1066	1201	1328
Solubility ...	0·834	0·831	0·829	0·829	0·828	0·828

Concentration, 0·464. Density, 0·999.

Pressure......	740	839	931	1075	1216	1345
Solubility ...	0·866	0·859	0·854	0·849	0·845	0·845

Concentration, 0·759. Density, 1·000.

Pressure......	734	833	928	1070	1211	1337
Solubility ...	0·894	0·888	0·875	0·869	0·862	0·859

These results again yield a solubility curve similar to that for methyl-orange.

The initial absorption of gas caused the separation of a slight precipitate, which dissolved as the absorption proceeded, partly in the case of the more concentrated solutions, and entirely in the case of the more dilute solutions. In the most dilute solutions no precipitate was formed.

II.—*Solubility of Hydrogen.*

The solubility of hydrogen in solutions of dextrin, starch, gelatin, ferric hydroxide, and in the presence of a suspension of metallic silver was determined in order to compare the behaviour of a sparingly soluble gas with that of the more soluble gases, carbon dioxide and nitrous oxide. The hydrogen was prepared by the electrolysis of dilute sulphuric acid.

In connexion with these determinations the difficulty was met with that the error of experiment was comparatively large, about 1·5 per cent., even when several special precautions were introduced in the working. Within the limits of this error it was found that the solubility of hydrogen in the solutions mentioned was in all cases, with the possible exception of the solutions of gelatin, in harmony with Henry's law. In the case of the hydrosol of ferric hydroxide and the suspension of silver, the solubility of hydrogen was not appreciably different from that in water.

The following are the main results obtained:

(*a*) *Solubility in Water:*

Pressure......	757	850	992	1095	1252	1380
Solubility ...	0·0198	0·0200	0·0198	0·0195	0·0196	0·0196
Pressure......	756	877	986	1097	1244	1393
Solubility ...	0·0199	0·0193	0·0194	0·0197	0·0202	0·0198

The mean value of all determinations was 0·0197, in excellent agreement with the value obtained by other investigators.

(*b*) *Dextrin:*

Concentration.	Density.	Solubility of CO_2.
3·98	1·012	0·0194
5·59	1·019	0·0191
8·12	1·028	0·0188
19·20	1·066	0·0174

(*c*) *Starch:*

Concentration.	Density.	Solubility of CO_2.
2·01	1·005	0·0194
3·56	1·011	0·0189
7·13	1·024	0·0181
9·29	1·032	0·0182

(*d*) *Gelatin:*

Concentration, 1·53. Density, 1·002.

Pressure......	753	862	1002	1103	1248	1384
Solubility ..	0·0194	0·0188	0·0193	0·0195	0·0195	0·0194

Concentration, 2·69. Density, 1·005.

Pressure......	746	868	987	1101	1245	1380
Solubility ...	0·0189	0·0185	0·0189	0·0190	0·0189	0·0191

Concentration, 4·72. Density, 1·011.

Pressure......	753	864	999	1112	1255	1395
Solubility ...	0·0185	0·0181	0·0186	0·0186	0·0186	0·0185

Concentration, 5·71. Density, 1·015.

Pressure......	750	866	975	1098	1244	1383
Solubility ...	0·0182	0·0173	0·0183	0·0184	0·0181	0·0183

It will be observed that here a slight but distinct minimum of solubility occurs.

Discussion of Results.

In the previous communication on this subject it was shown that the solubility of carbon dioxide and nitrous oxide in water in presence of colloids is sometimes greater, sometimes less, than the solubility in pure water; but that no matter whether the solubility is greater or less, it does not obey Henry's law. The results communicated in the present paper go to show that colloidal solutions are peculiar in this respect, the solubility of carbon dioxide in solutions of crystalloids being in harmony with Henry's law.

As the general question of the influence of crystalloids on the solubility of gases in water has been studied by others with a considerable degree of fullness, and as it did not form a main part of our investigation, we need not discuss further the results obtained by us; although we might point out that the exceptionally slight influence of chloral hydrate on the solubility of carbon dioxide is in harmony with the behaviour found by Knopp in the case of hydrogen. It may also be pointed out that if one refers the solubility not to the whole volume of the solution but merely to the water in the solution, it is found that in the case of the solutions of chloral hydrate the solubility of carbon dioxide is greater than in pure water; and this remains true, even when it is assumed that the water combined in the chloral hydrate is split off and acts like pure water in dissolving carbon dioxide. This is also in harmony with the behaviour found by Knopp in the case of hydrogen. An explanation of this behaviour still remains to be found.

It has previously been pointed out by Findlay and Creighton (Trans., *loc. cit.*; *Biochem. J.*, *loc. cit.*) that the solubility of carbon dioxide in the presence of colloids appears to be appreciably greater than in water only when chemical combination can be assumed; and it was shown that the solubility curve for carbon dioxide in solutions of ferric hydroxide was of the same form as that obtained with solutions of aniline, or that for the solubility of oxygen in blood. Further support for this view has been obtained by determining the solubility of carbon dioxide in solutions of methyl-orange, a salt which undergoes considerable hydrolysis in solution, and therefore acts as a weak alkali. In this case also the curve obtained is completely analogous to that obtained for the solubility of carbon dioxide in solutions of aniline.

Solubility of Carbon Dioxide in Solutions of Peptone, Propeptone, and Haemoglobin.—The solubility of carbon dioxide in these solutions is, as has been shown, greater than in water; and the solubility curve which is obtained is completely analogous to those obtained in the case of ferric hydroxide, aniline, and methyl-orange. This increased solubility, therefore, we are no doubt justified in ascribing to chemical combination. It would also appear that combination of the peptone, propeptone, and hæmoglobin with the carbon dioxide is practically complete at atmospheric pressure, as the following consideration shows. Assuming that no adsorption takes place, and that the colloid is neither hydrated nor exerts any specific influence on the solubility of the gas, we can readily calculate the volume of gas, V, which combines with the colloid from a determination of the solubility and a knowledge of the amount of water in a given volume of the solution. If we then subtract from the total volume of gas dissolved the volume V due to combination with the colloid, the difference gives the solubility in the water present in the solution. The following results are thus obtained (compare Findlay and Creighton, *Biochem. J.*, *loc. cit.*).

Peptone.

Concentration, 1·68. Density, 1·002. Water in solution, 69·29 c.c.
$V = 5·26$ c.c.

Pressure......	750	852	962	1092	1230	1353
Solubility ...	0·825	0·824	0 825	0·826	0·825	0·827

Propeptone.

Concentration, 0·80. Density, 0·999. Water in solution, 68·09 c.c.
$V = 2·02$ c.c.

Pressure......	743	842	935	1079	1219	1347
Solubility ...	0·825	0·826	0·825	0·824	0·826	0·827

Haemoglobin.

Concentration, 0·759. Density, 0·999. Water in solution, 69·57 c.c.
$V = 2·78$ c.c.

Pressure......	734	833	928	1070	1211	1337
Solubility ...	0·825	0·827	0·822	0 824	0·823	0·824

Since in all these cases the value of the solubility is the same as in pure water, it would appear that the increased solubility of carbon dioxide in the solutions of the above substances can be accounted for on the basis of chemical combination. This conclusion, if correct, should be of some importance in connexion with the physiology of the blood; but it must be said that no compound of hæmoglobin and carbon dioxide has as yet been isolated. The brown precipitate which is thrown out of solution during the first stages of absorption of carbon dioxide is presumably identical with that obtained by Schultz (*Zeitsch. physikal. Chem.*, 1898, **24**, 449) by treating a solution of hæmoglobin with a small quantity of hydrochloric acid, the precipitate redissolving in excess of the acid. This would indicate that hydrolysis of the hæmoglobin into hæmatin and globin occurred during the absorption of carbon dioxide, and was brought about by the carbonic acid. It is, of course, known that carbonic acid gradually changes hæmoglobin into methæmoglobin (Harnack, *Zeitsch. physiol. Chem.*, 1899, **26**, 571), and we may find in these reactions the explanation, or a partial explanation, of the increased solubility of carbon dioxide in solutions of hæmoglobin.

Solubility of Hydrogen.—With regard to the solubility of hydrogen in presence of colloids our results are not sufficiently definite to warrant the drawing of conclusions. So far as our experiments go they do not indicate that pressure has any influence on the solubility of hydrogen in any of the solutions, except possibly the solutions of gelatin. Our apparatus was, however, too inaccurate to enable one to detect the comparatively small changes in solubility which are all that one could expect to take place. Recently Drucker and Moles (*Zeitsch. physikal. Chem.*, 1910, **75**, 405) have used a more accurate apparatus for studying solubilities of sparingly soluble gases, but it is doubtful if even their apparatus is sufficiently sensitive.

The presence of ferric hydroxide and of finely divided silver in suspension exerts no appreciable influence on the solubility of hydrogen. In the case of the other substances investigated, the solubility decreases with increase in the concentration of the solution. On referring the solubility merely to the water present, however, the influence of the colloid appears negligible.

Summary.

(1) The solubility of carbon dioxide in solutions of ammonium chloride, potassium chloride, barium chloride, ferrous ammonium sulphate, sucrose, and chloral hydrate is in harmony with Henry's law.

(2) The solubility of carbon dioxide in solutions of peptone, propeptone, and hæmoglobin is greater than in water, but decreases as the pressure is increased. This behaviour is explained on the basis of chemical combination.

(3) The solubility of hydrogen in solutions of dextrin, starch, gelatin, ferric hydroxide, and in a suspension of silver is, with the possible exception of the solutions of gelatin, in harmony with Henry's law.

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CLVII.—*A Theory of Fluorescence.*

By EDWARD CHARLES CYRIL BALY and RUDOLF KRULLA.

IN forming any theory as regards the many phenomena that have been recorded of absorption, fluorescence, and phosphorescence, more especially of the very profound influence of the solvent, it is evident that some account must be taken of the residual affinity of the substances that are concerned. Although, however, the term residual affinity has frequently been used to explain many chemical processes, yet no satisfactory and connected explanation has been brought forward as to the nature and origin of this property. It is generally accepted that the formation of compounds such as hydrates and double salts are due to the secondary valencies of the atoms of the compounds concerned, and that every elementary atom possesses these secondary valencies to a greater or less extent. In any compound that is formed by virtue of the primary valencies of its atoms only, the secondary valencies are unsatisfied or unsaturated. Every atom must therefore be the centre of a field of force, the nature and strength of which depends on the nature of the secondary valencies in each case. In addition to the unsaturation of the secondary valencies, we must add the unsaturation of the primary valencies when this is known to exist. Clearly therefore each atom in a compound must be the centre of a field of force the lines of which radiate in every direction.

Now the independent existence of the several fields of force in any one molecule must be a metastable condition, for the lines of force of the several fields must condense together with the escape of free energy. The result of this condensation will be the production of a closed system of force lines, and the free affinities of the molecule will be considerably reduced. When the condensation of the force lines has occurred it is not necessary that the whole of the free affinities should disappear, for this will only take place when there is a perfect equality between those of opposite type within the molecule. In those cases when there is not a perfect equality there will naturally be left a balance of affinity, and it is this balance which should be defined by the term "residual affinity," and this term should mean that amount of affinity left uncompensated after the maximum condensation between the various force fields has occurred. This residual affinity of a molecule may be of positive or negative, or, as more usually called, basic or acid, type according to the conditions obtaining within that molecule.

Again, it is evident that the chemical reactivity of a molecule must depend on the free affinity which exists, and it is a necessary deduction that the condensing together of the lines of force must result in a decrease of chemical reactivity, and, indeed, it would seem to follow that the true chemical reactivity of any molecule cannot be exhibited until the condensed systems of force lines within each molecule have been unlocked or opened by some means.

The application of this conception to chemical reaction and its bearing on catalysis need not be dealt with here, and in the following pages it is shown how the phenomena of light absorption and fluorescence may be explained by its means.

In dealing with the methods of opening the closed systems, it is clear that this may be brought about if free energy is supplied to them. Many reactions are catalysed by the action of light, and it may be concluded that the light opens the closed systems so that the free affinities of the molecules are brought into play and the reaction between them can take place. The necessary free energy is supplied by the light, and this gives us at once a rational explanation of the absorption of the light. The light is doing work against the chemical forces which tend to produce the closed systems, and as a result we find that the light is selectively absorbed, only those rays being absorbed which suit the particular closed system examined. The action of the light is to bring the substance from a lower to a higher energy content, and owing to the damping that must be present, the effect is produced of a continued absorption of the light vibrations. At the same time, it cannot be assumed that every pure substance must exert selective absorption of light, for it by no means follows that every closed system can be opened by the influence of light alone. In fact, several substances in the pure state have been shown by Purvis not to exhibit selective absorption, although they do so when dissolved in some suitable solvent. It is obvious from this that some substances are not opened by light alone, but are so opened when light acts on their solutions.

If now the admixture of a second substance be considered, such as occurs when the closed system is dissolved in some solvent, then the residual affinity of the second substance will come into play. There will exist throughout the mass of the solvent a force field due to the residual affinity, and when a substance is dissolved in it the force lines will tend to penetrate the closed force field of the solute, with the result that it will be partly or completely opened, and the amount of opening that takes place will depend on the relation between the affinities of the two and on the relative masses of the two, solvent and solute. The greater the difference between the residual affinities, the more will the closed system of the solute be opened, and, again, the closed system will be the more opened the greater the mass of the solvent, that is, the greater the dilution. The reason why certain substances in a pure state show no selective absorption of light and yet do so in solution is due to the fact that in the pure state the light cannot do any work on them, but in solution their systems are sufficiently opened for the light to do work, with the result that it is selectively absorbed.

The necessary variation in the opening up of the closed systems with dilution in any one solvent at once gives an explanation why Beer's law fails to hold in so many cases. The progressive variation from Beer's law in the light of this theory will be discussed in a later paper.

It must not be forgotten that in the case of a solution of one substance in another the penetration and opening of the closed field of the solute by the force lines of the solvent produces a system of solvent and solute which is known as a solvate, and it is on this solvate that the light acts. The variations in the wave-length of the light that is absorbed by the same substance in different solvents are due to this cause, the variations being caused by the differences in the residual affinities of the solvents. Kundt's rule therefore should read that the absorption band of a substance is shifted more towards the red the greater is the relative residual affinity of the solvent, not the greater is its index of refraction. This rule is only true within certain limits, as will be shown below.

It may be pointed out here that the formation of the systems of solvent and solute or solvates may be regarded as chemical reactions in embryo. Such systems must possess within themselves potential gradients, and may be looked upon as loose molecular complexes formed by the secondary valencies of the substances concerned. If, however, the affinities of the two, solvent and solute, are sufficiently great and sufficiently different, the potential gradient within the combined system may be sufficiently steep for the electrons to rearrange themselves, with the result that a true chemical reaction will take place. There would seem therefore to be no necessity to conceive any break in the continuity between true chemical reaction and the simple mutual influence between solvent and solute. Finally, it may be said that in the extreme case of the opening up of the closed system by a solvent, it can be considered as having been resolved into two or more independent entities, so that ionic dissociation would seem to be a particular case of the whole.

In dealing with the mechanism of the opening up of the closed system, it cannot be assumed in general that this only takes place in one stage. Certainly, when large molecules are concerned, the condensed force fields of which must be very complicated, there must be several stages between the normal completely condensed system and the metastable condition when the system is entirely opened up. A well-known case, for example, of a molecule that is opened in two stages is that of the complex salt, $KAg(CN)_2$, which is first ionised into K′ and $Ag(CN)_2$, and then the anion undergoes a second stage, whereby free Ag′ ions are produced. In organic chemistry there are the cases of the amino-aldehydes and -ketones of the aromatic series, which are opened up in one stage by means of alcohol, and a second and further stage of opening is brought about by the addition of small quantities of alcoholic hydrogen chloride (Baly and Miss Marsden, Trans., 1908, **93**, 2108).

This being so we may denote the various stages in the opening up by the figures 1, 2, 3 . . . without making any assumption as regards the number of such stages between the closed substance in the free state 1 and the completely opened metastable stage. From what has gone before we see that 1 may be converted into 2 by the influence of light, certain rays being selectively absorbed in the process. Let these rays have a wave-length λ_2. By the influence of light and a second solvent we may open the substance into 3; the light of a different wave-length now will be absorbed, and let the wave-length of this be λ_3.* So far as experiment shows, λ_3 is greater than λ_2. Now clearly if the passage from 2 to 3 be brought about by the absorption of light of wave-length λ_3, the converse must be true, and the passage from 3 to 2 must be accompanied by the emission of light of wave-length λ_3. If now by the absorption of light of wave-length λ_2 the substance be converted from 1 to 2, it is impossible to conceive, since 2 and 3 are intimately connected, that 2 can return to 1 without influencing the lines of the whole system. One portion of a closely interwoven system of force lines cannot be opened without the whole being affected, and therefore the process $1 \rightleftharpoons 2$ must disturb the whole system. Now the next possible stage in the opening up process is 3, and the restoration of the system disturbed by the absorption of light of wave-length λ_2 must involve the system 3. Now it has already been shown that the process $3 \longrightarrow 2$ must be accompanied by emission of light of wave-length λ_3, and therefore when by the influence of light of wave-length λ_2 the substance is converted into 2, the process will be accompanied by the emission of some light of wave-length λ_3. In other words, the substance will fluoresce.

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* In reference to the statement that Kundt's rule even when modified as suggested only holds within limits, it is evident that it can only hold for those solvents which open up the condensed system of the solute to the same stage.

Of course, if there are several stages in the opening up process subsequent to 3, the stage 3 need not be the only one concerned. These subsequent stages may also be brought into play with the attendant emission of their peculiar wave-lengths of light, λ_4, λ_5, etc., provided that these stages are all intimately connected together. Such a phenomenon does not seem to have been observed in the fluorescence of organic substances unless the banded fluorescence of such substances as anthracene is due to this cause. It must be remembered that the intensity of emission will fall rapidly from stage to stage, and therefore the fluorescence of the higher stages will be relatively very weak. In the phosphorescence of minerals, where the same explanation doubtless holds good, there appear to be present bands due to several stages in the opening up. In connexion with the application of this conception to phosphorescence, the reason why pure substances do not phosphoresce under the influence of cathode rays becomes clear. The condensed systems of the substances are not capable of being opened by the cathode rays, but they absorb them when they are in a state of solid solution in the so-called "diluent." Again, the maximum of phosphorescence observed at a particular concentration of the phosphorogen in the diluent is no doubt due to the fact that at this concentration the closed system of the phosphorogen is opened up sufficiently for the maximum absorption of the energy of the cathode rays, with the result that a maximum of phosphorescence is exhibited.

In reference to the above theory we have made certain observations that seem to afford it strong support. It was stated above how the aromatic amino-aldehydes and -ketones are opened up to two different stages, one in alcoholic solution and the other in presence of a small quantity of alcoholic hydrogen chloride. It follows from what was said above, if these two stages be called 2 and 3 respectively, and the light absorbed be λ_2 and λ_3 respectively, that these compounds should, when in stage 1 and absorbing light of wave-length λ_2, fluoresce with emission of light of wave-length λ_3, for it is clear that the fluorescence emission due to stage 3 should correspond with the absorption of the compound when being opened to stage 3. We find that this relation holds good, and that the amino-aldehydes and -ketones in alcoholic solution and absorbing light of wave-length λ_2 emit fluorescent light of wave-length λ_3, which is the same as that absorbed by these compounds in presence of small quantities of alcoholic hydrogen chloride. The following are the values obtained for the wave-lengths of λ_3 for the particular substance, both when fluorescing and when absorbing:

Substance.	Light absorbed in presence of small amounts of hydrochloric acid.	Fluorescent light emitted in alcoholic solution.
o-Aminobenzaldehyde	λ = 500 to λ = 435 maximum λ = 465	λ = 495 to λ = 455 maximum λ = 465
p-Dimethylaminobenzaldehyde	λ = 492 to λ = 411 maximum λ = 463	λ = 476 to λ = 417 maximum λ = 455
pp'-Tetramethyldiaminobenzophenone	λ = 555 to λ = 455 maximum λ = 495	λ = 481 to λ = 454 maximum λ = 470

In the last compound the fluorescence was very faint, and would undoubtedly extend further towards the red with longer exposures. The agreement between the two is eminently satisfactory.

It has also occurred to us that very possibly a similar explanation would apply to the cases of compounds like triphenylcarbinol, which develop such striking colours when dissolved in concentrated sulphuric acid. These colours would seem to be due to the opening up of the condensed systems of these compounds to a further stage. If this is true the wave-length of the light absorbed by the sulphuric acid solution will be the same as that emitted as fluorescence by the alcoholic solution. We find that this relation also holds good in the case of triphenylcarbinol, and that the emitted light in the one case and the absorbed light in the other are almost exactly the same. The wave-lengths observed were as follows, the absorption exerted by the sulphuric acid solution being taken from Baker's paper (Trans., 1907, **91**, 1490):

Light absorbed by concentrated sulphuric acid solution.	Fluorescent light emitted by alcoholic solution.
λ = 500 to λ = 313	λ = 476 to λ = 400
maximum λ = 457	maximum λ = 435

The agreement is extremely good, and justifies the application of the theory to this type of compound. There is no reason to postulate the existence of the semi-quinonoid formula to account for the colour of these compounds in concentrated sulphuric acid, for example:

Indeed, the quinonoid structure cannot be taken as an explanation of the colour (Baly, Tuck, and Miss Marsden, Trans., 1910, **97**, 571, 1494), but we feel that the true explanation lies in the fact that the condensed systems of the compounds are opened to a further stage in the sulphuric acid with the absorption of light of greater wave-length.

In conclusion, we have to express our thanks to the Chemical Society for a grant in aid of the work.

UNIVERSITY COLLEGE LONDON, AND
THE UNIVERSITY OF LIVERPOOL.

CLVIII.—*Chemical Reactivity and Absorption Spectra. Part I.*

By Edward Charles Cyril Baly and Francis Owen Rice.

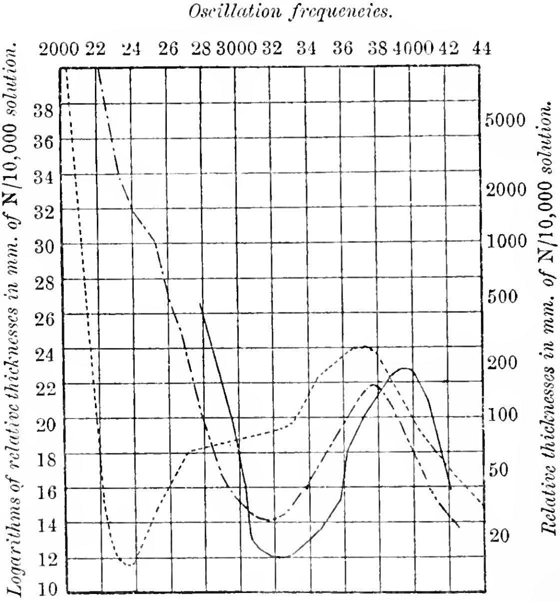
In the preceding communication the conception of condensed systems of force lines around the molecules arising from the unsaturated primary and secondary valencies of the constituent atoms was applied to the phenomena of fluorescence and phosphorescence. In the present paper it is proposed to deal with it in reference to the mechanism of chemical reaction. It is evident from what has been said in the previous paper that the condensing together of the lines due to the force fields round the component atoms of a molecule must result in an enormous decrease in the reactivity of the molecule, and, in fact, it may be said that such a condensed system cannot react unless it previously be opened or unlocked by some means; for example, the well known cases described by Baker when pure dry substances such as ammonia and hydrogen chloride, lime and carbon dioxide, do not react together are doubtless due to the fact that the force fields of the molecules are so condensed together that no reaction takes place when they are brought together. The presence of water is required in order to open these systems sufficiently for the reaction to proceed, the merest trace of water being enough to catalyse the whole reaction. Again, the converse cases of the vapours of ammonium chloride and mercurous chloride may be explained in the same way, for these molecules evidently possess their force-fields so condensed that increase of temperature alone is not sufficient to open them, and the vapour densities correspond with those of the undissociated molecules.

The presence of water, however, opens the condensed fields sufficiently for the molecules to dissociate under the influence of higher temperatures.

The general phenomenon of catalysis is capable of explanation on these lines, for a catalytic agent may be defined as one which opens the condensed system of the reacting substance or substances so that their chemical reactivity is enhanced. Negative catalysis is equally capable of explanation, for a negative catalyst is simply a type of substance which tends to close up the condensed systems, and thus counteract the action of the solvent. Specific evidences of such closing of the molecular systems have been observed from absorption spectra, as will again be mentioned.

It follows from the above that any chemical reaction must take place in at least two stages. First, the reacting substances must have their condensed systems opened up, and secondly, these opened systems will react together to give the expected compound. It is clear that these stages should be possible of observation, and that in the event of their taking place they should evidence themselves in some way. There is no doubt that the explanation of the colour changes of the aromatic amino-aldehydes and -ketones when treated with alcoholic hydrogen chloride are due to these stages in the reaction. When, for example, *o*-aminobenzaldehyde is dissolved in alcohol, the condensed system is partly opened owing to its penetration by the force lines due to the residual affinity of the alcohol. On the addition of hydrogen chloride the final product is, of course, the hydrochloride, but the base in the form in which it exists in alcoholic solution does not itself react with the acid to give the salt. It passes through an intermediate phase when it is opened up to a more complete stage, and it is this intermediate phase that reacts with more acid to form the salt. The intermediate phase has a yellow or red colour with a characteristic absorption band as

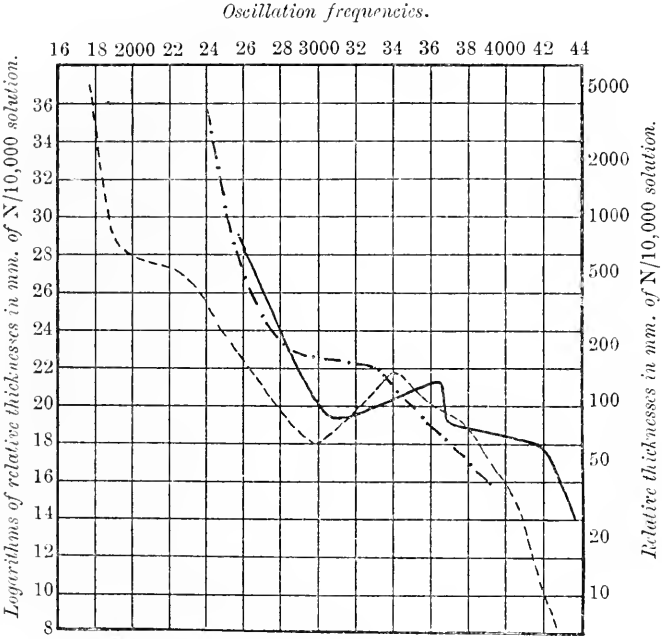
Fig. 1.



Full curve : p-*Nitroanisole in alcohol.*
Dotted curve : ,, ,, *sulphuric acid.*
Dot and dash curve : ,, ,, ,, ,, *after warming.*

has already been described (Baly and Miss Marsden, Trans., 1908, **93**, 2108). Although these aromatic aldehydes and ketones behave as the theory leads us to expect, yet, owing to the fact of their basicity being so pronounced, it is not possible to convert them all into the intermediate phase. We felt, therefore, that it would be more satisfactory to investigate other organic reactions, and we have found that the sulphonation of the benzene ring is an excellent case in which the intermediate opened-up phase can be recognised.

Fig. 2.

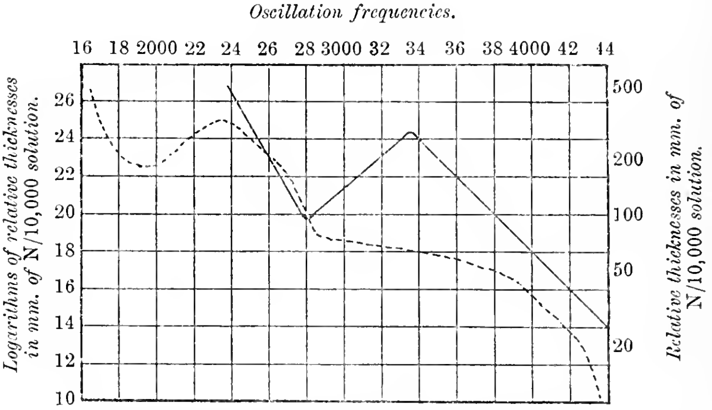


Full curve : o-*Nitroanisole in alcohol.*
Dotted curve : ,, ,, *sulphuric acid.*
Dot and dash curve : ,, ,, ,, ,, *after warming.*

The first case investigated was *p*-nitroanisole, and in Fig. 1 are shown the absorption curves of this substance in alcohol and in concentrated sulphuric acid. In the former case the condensed system is only opened up to one stage, whilst in the second case the system is more completely opened up to a second stage, the absorption in this case being that of the intermediate phase, which then proceeds to react and give the sulphonic acid. This solution on keeping for some hours at 80° changed into one of the sulphonic acid, the absorption now being shown by the dot and dash curve in Fig. 1. It seems to us that in this observation a more complete proof of the theory is to be found than with the amino-aldehydes, because here we have evidence that the whole of the *p*-nitroanisole is converted into the intermediate phase, which may clearly be recognised by the spectroscope before the sulphonic acid is formed.

In Fig. 2 are shown the absorption curves of *o*-nitroanisole in alcohol and concentrated sulphuric acid, whilst the dot and dash curve is that of the sulphonic acid, which is produced on allowing the sulphuric acid solution to remain for three hours at 80°. In this case the presence of the intermediate phase is clearly marked by the step-out in the absorption curve, but we have not found it possible to convert the whole of the *o*-nitroanisole into the intermediate phase owing to the comparative readiness with which it reacts to give the sulphonic acid.

Fig. 3.



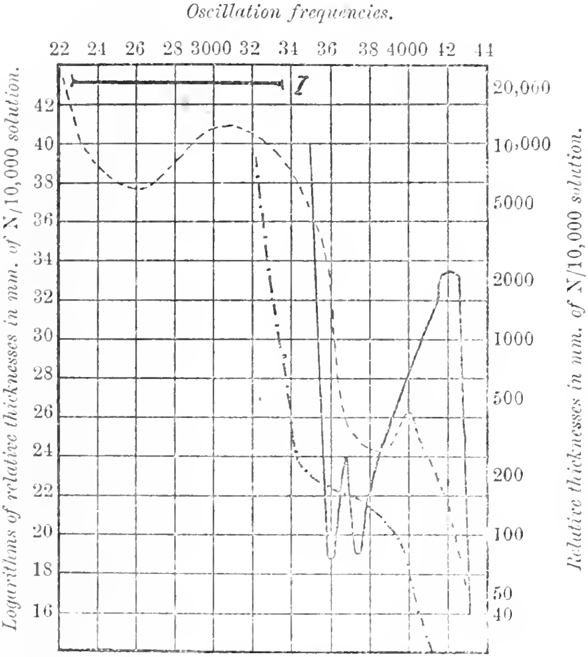
Full curve : *Nitroquinol dimethyl ether in alcohol.*
Dotted curve : ,, ,, ,, *sulphuric acid.*

We have also examined nitroquinol dimethyl ether, the absorption curves of which in alcohol and concentrated sulphuric acid are shown in Fig. 3. Unfortunately, the sulphuric acid solution on allowing to remain at 80° showed so much evidence of charring that it was impossible to photograph its absorption spectrum. In this case, again, there is very distinct evidence of the intermediate phase.

We have also examined anisole, and the dimethyl ethers of resorcinol and quinol with the same results. As may be seen on reference to the curves in Figs. 4, 5, and 6, these three substances are sulphonated with great ease, but in spite of this we were able to obtain the absorption of the intermediate phase in each case by the use of sulphuric acid containing 20 per cent. of water.

Now in dealing with the actual mechanism of the reaction considered above, it must be remembered that when the substance is dissolved in the sulphuric acid its condensed system is opened up by being penetrated by the force lines due to the residual affinity of the acid. There is thus formed a system of solute and acid which by rearrangement is converted into the sulphonic acid. The essential point to be noted is that in this system the condensed field of the organic compound is opened up. Within this system there must exist a potential gradient, and this gradient causes the electrons to rearrange themselves, and this rearrangement in the case of anisole, for example, may be expressed as follows:

FIG. 4.



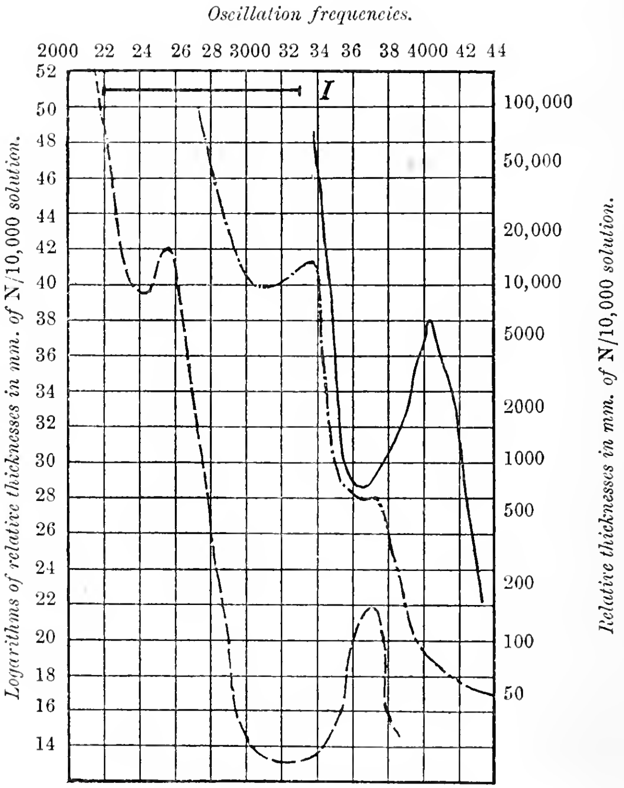
Full curve : *Anisole in alcohol.*
Dotted curve : ,, ,, *sulphuric acid.*
Dot and dash curve : ,, ,, ,, ,, *after keeping.*

$$CH_3{\cdot}O{\cdot}C_6H_5,H_2SO_4 = CH_3{\cdot}O{\cdot}C_6H_4{\cdot}SO_3H,H_2O.$$

In passing, it may be said that any molecular transformation whatsoever may be looked upon simply as a rearrangement of the electrons due to the potential gradient within the condensed system of force lines of the molecule being sufficiently steep.

Of the above compounds, anisole and the dimethyl ethers of resorcinol and quinol are fluorescent in alcoholic solution. According to the theory of fluorescence put forward in the previous paper, the wave-lengths of the light emitted by each substance in fluorescence should be the same as the wave-lengths of the light absorbed by that substance in sulphuric acid solution when its condensed system is opened up. We have photographed the fluorescence of these three compounds, and find that the agreement demanded by the theory holds good, for the fluorescent light extends over the region of the absorption band in the sulphuric acid solution. The

Fig. 5.

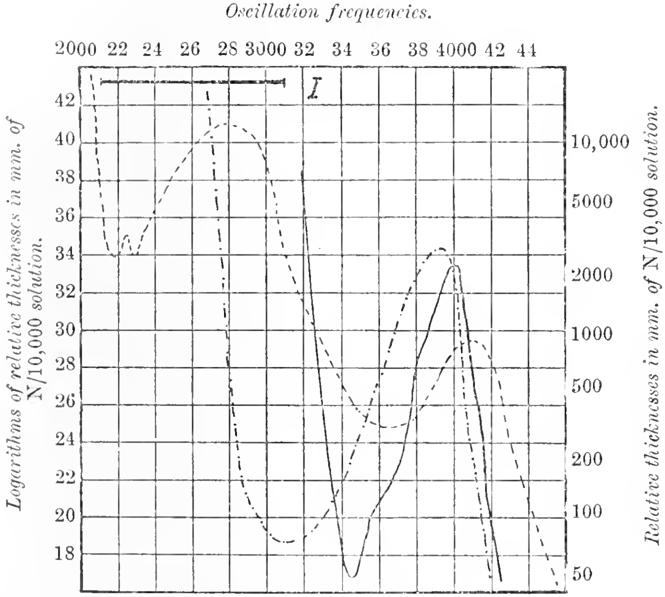


Full curve: *Resorcinol dimethyl ether in alcohol.*
Dotted curve: ,, ,, ,, *sulphuric acid.*
Dot and dash curve: ,, ,, ,, ,, ,, *after keeping.*

extent of the fluorescent spectrum is indicated by the thick line (I) shown above the absorption band of the sulphuric acid solution in each of the three cases.

It will be noticed that the fluorescent spectrum extends more towards the ultraviolet than the absorption band in each case. This is, however, only to be expected, for the absorption bands only represent the presence of a relatively small amount of the intermediate opened-up phase. If the whole of the particular compound were opened up into the intermediate phase, the type of

Fig. 6.



Full curve : *Quinol dimethyl ether in alcohol.*
Dotted curve : ,, ,, ,, *sulphuric acid.*
Dot and dash curve : ,, ,, ,, ,, ,, *after warming.*

absorption would resemble that of *p*-nitroanisole in sulphuric acid. The region covered by the absorption band would then extend much further towards the ultraviolet.

We would point out that the fluorescent spectrum of anisole as measured by us does not agree with that given by Ley and Engelhardt (*Zeitsch. physikal. Chem.*, 1910, **74**, 1). The values given above were first obtained by Dr. Krulla and one of us in London, and we have now confirmed them. The fluorescence spectra of the dimethyl ethers of resorcinol and quinol as given above also represent the means of two observations of each. All these observations were made with the iron arc as the exciting source, which owing to its emitting many more rays than the mercury lamp as used by Ley and Engelhardt is probably more satisfactory.

We have also attempted to obtain the opening up of hydrocarbons such as benzene and the xylenes, but in every case it was found that the substance was sulphonated at once on solution. Up to the present, therefore, we have not been able to obtain the opened-up stages of the hydrocarbons, the absorption bands of which should be in the same spectral region as the fluorescence of their alcoholic solutions.

In conclusion, we have again to thank the Chemical Society for a grant in aid of this work.

THE UNIVERSITY, LIVERPOOL.

CLIX.—*Contributions to our Knowledge of Semicarbazones. Part I. Semicarbazones of Phenyl Styryl Ketone.*

By ISIDOR MORRIS HEILBRON and FORSYTH JAMES WILSON.

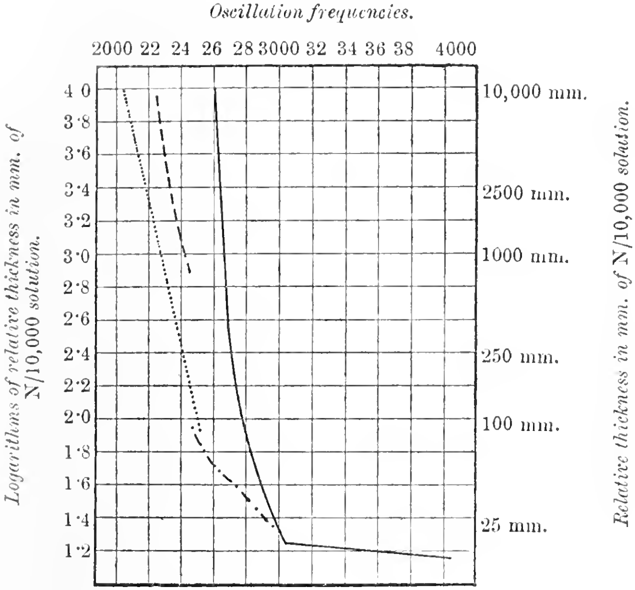
IN a recent paper (Proc., 1911, **27**, 325) it was shown that the semicarbazones of phenyl styryl ketone exist in several modifications. By the action of semicarbazide acetate on phenyl styryl ketone a white semicarbazone (m. p. 168°), which we designate the α-modification, and a yellow semicarbazone (β-modification) were obtained. The β-modification on recrystallisation, or even on moistening with a solvent, passes without change of weight into another white semicarbazone (m. p. 179—180°) (γ-modification), which in its turn is reconverted by light into the β-modification.

These semicarbazones have been more fully investigated, and form the subject of the present paper.

The α- and γ-modifications in alcoholic solution assume a deep yellow colour on addition of sodium ethoxide. The absorption spectra of the alcoholic solutions of the α- and γ-semicarbazones with and without sodium ethoxide were investigated, in each case three solutions being examined: $N/100$, $N/1000$, $N/10{,}000$. Fig. 1 shows the absorption curve of the α-modification (full curve), Fig. 2 the γ-modification (full curve). The dash curve in both figures represents the effect of 1 molecule and of 10 molecules of sodium ethoxide on the respective semicarbazones, a shift of about 300—400 units towards the red taking place in the $N/100$-solutions.

In the more dilute solutions very marked deviations from Beer's law occur, the curves coinciding with those of the semicarbazones themselves. The dotted curves in both figures show the effect of 100 molecular proportions of sodium ethoxide on the semicarbazones, a further shift towards the red taking place, whilst the deviation from Beer's law occurs at a greater dilution, being produced in the $N/10,000$-solutions. The dot-dash curve in Fig. 1 represents the effect of 200 molecular proportions of sodium ethoxide on the α-semicarbazone. It will also be seen that the absorption curves of the α- and γ-modifications show a general resemblance to one another, a shallow band being present at 3000—3700 in the case of the γ-semicarbazone, whilst with the α-semicarbazone a very rapid extension of the spectrum takes place at the same dilution.

Fig. 1.

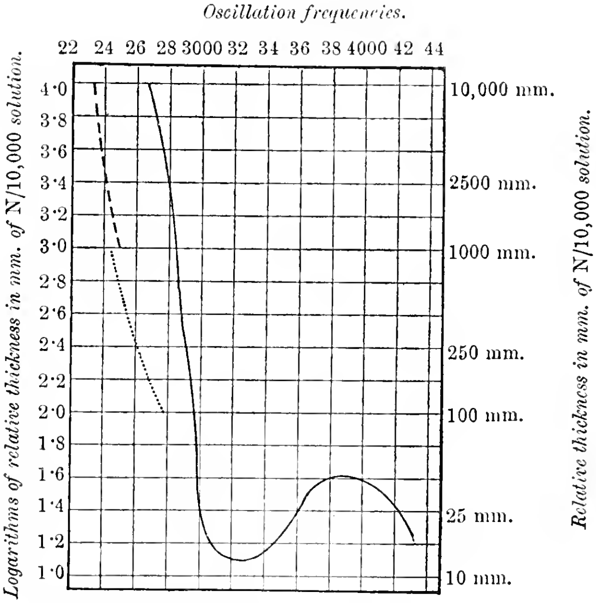


α-Semicarbazone (full curve).
α-Semicarbazone + 1 *mol. sodium ethoxide* (dash curve).
,, +100 ,, ,, (dot curve).
,, +200 ,, ,, (dot-dash curve).

Salt-formation between the sodium ethoxide and the semicarbazones is, from a purely chemical point of view, extremely improbable, and is rendered still more so from the study of the absorption spectra, as is shown by the continued shifting towards the red with increasing quantities of sodium ethoxide and the conspicuous deviations from Beer's law.

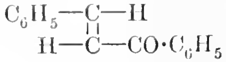
The most probable explanation of the above facts appears to us to be in the assumption that the α- and γ-semicarbazones are converted on addition of sodium ethoxide into stereoisomerides, the ethoxide solutions containing equilibrium mixtures of the colourless and yellow isomerides, the quantity of the yellow isomerides increasing with increasing amounts of ethoxide. Probably the yellow β-stereoisomeride is present in the ethoxide solution of the γ-modification, although unfortunately this point cannot be proved, as no yellow form could be isolated from the ethoxide solution, and the β-modification could not be dissolved in a non-alkaline solvent without passing into the γ-form.

FIG. 2.



γ-*Semicarbazone* (full curve).
γ-*Semicarbazone* + 10 *mol. sodium ethoxide* (dash curve).
" +100 " " (dot curve).

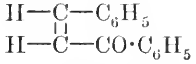
The ethoxide solution of the α-semicarbazone will contain, then, a fourth isomeride (δ-modification) only stable in presence of alkali, since from this solution the α-semicarbazone is always regenerated in attempting to obtain the δ-form. According to current views on stereoisomerism, phenyl styryl ketone should be capable of existence in two forms:



$$\begin{array}{l} C_6H_5-C-H \\ \qquad\quad \| \\ \quad H-C-CO\cdot C_6H_5 \end{array}$$

(I.)

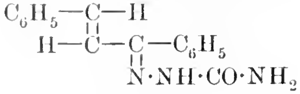
and



$$\begin{array}{l} H-C-C_6H_5 \\ \qquad \| \\ H-C-CO\cdot C_6H_5 \end{array}$$

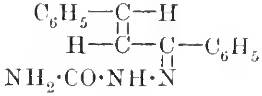
(II.)

and each of these forms should, according to the Hantzsch-Werner hypothesis, give two semicarbazones:



$$\begin{array}{l} C_6H_5-C-H \\ \qquad\quad \| \\ \quad H-C-C-C_6H_5 \\ \qquad\qquad\ \ \| \\ \qquad\qquad N\cdot NH\cdot CO\cdot NH_2 \end{array}$$

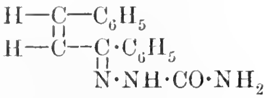
(I*a*.)



$$\begin{array}{r} C_6H_5-C-H\qquad\quad \\ \| \qquad\qquad \\ H-C-C-C_6H_5 \\ \| \qquad\quad \\ NH_2\cdot CO\cdot NH\cdot N \qquad\qquad \end{array}$$

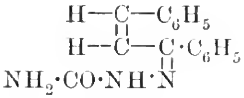
(I*b*.)

and



$$\begin{array}{l} H-C-C_6H_5 \\ \qquad \| \\ H-C-C\cdot C_6H_5 \\ \qquad\qquad \| \\ \qquad\qquad N\cdot NH\cdot CO\cdot NH_2 \end{array}$$

(II*a*.)



$$\begin{array}{r} H-C-C_6H_5\qquad \\ \| \qquad\qquad \\ H-C-C\cdot C_6H_5 \\ \| \qquad\quad \\ NH_2\cdot CO\cdot NH\cdot N \qquad\qquad \end{array}$$

(II*b*.)

so that altogether four stereoisomeric semicarbazones are theoretically possible.

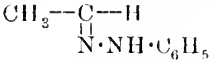
That the α-, β-, and γ-forms are true semicarbazones is proved by their hydrolysis with acid, phenyl styryl ketone being regenerated in each case.

The stereoisomerism of the α- and γ-modifications is rendered evident from the following considerations: Dimorphism is excluded as each form is permanent in solution, and a mixed melting-point determination of the two forms shows a considerable depression.

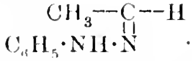
Polymerism is also excluded as molecular-weight determinations of both modifications give normal results. That, however, a connexion between the α- and the γ-forms exists is evident by their behaviour when exposed for some length of time to ultraviolet light which brings about a mutual conversion; this in itself practically deciding the stereochemical relation of the two semicarbazones.

As regards the β- and γ-forms, the only probability apart from stereoisomerism is dimorphism. This, however, is very unlikely from the fact that with many of the unsaturated ketones and aldehydes, which we have at present under examination, colourless semicarbazones have been obtained which become intensely yellow on exposure to light, and form yellow solutions when dissolved in alcohol on addition of sodium ethoxide. That, moreover, the β- and γ-forms are not merely dimorphous is shown by the fact that the crystals of this pair are identical according to measurements made by Dr. A. Hutchinson, M.A., of Pembroke College, to whom our best thanks are due.

It was found by Laws and Sidgwick (Trans., 1911, **99**, 2085) that the isomeric acetaldehydephenylhydrazones:



$$\begin{array}{l}CH_3-C-H\\ \quad\;\;\, \| \\ \quad\;\;\, N\cdot NH\cdot C_6H_5\end{array}$$



$$\begin{array}{r}CH_3-C-H\\ \| \quad\;\; \\ C_6H_5\cdot NH\cdot N \quad\;\;\end{array}.$$

can be converted into one another by solvents containing a trace of acid or alkali, one form being stable in presence of alkali and the other in the presence of acid. This phenomenon is somewhat analogous to the transformation of the α- and γ-semicarbazones into the δ- and β-forms respectively by the action of sodium ethoxide. In the case of the phenylhydrazones the stereoisomerism is due solely to the alteration in position of the $\dot{:}N\cdot NH\cdot C_6H_5$ residue. From analogy to the acetaldehydephenylhydrazones, and owing to their very close relation, we are inclined to the view that the β- and γ-forms are related to one another, either as I(*a*) and I(*b*) or II(*a*) and II(*b*), as given previously.

Forster and Zimmerli (Trans., 1910, **97**, 2156) obtained two stereoisomeric semicarbazones from camphorquinone, one colourless and one yellow. According to them, the coloured form is the one in which there is the closest massing together of unsaturated groups. From analogy, we suggest that possibly formula II(*a*), where there is the closest grouping of unsaturated residues, represents the stable yellow β-semicarbazone, II(*b*) representing the γ-form, which is so easily obtained from the β-form. From this point of view formula I(*b*) would represent the α-semicarbazone, and I(*a*), where the grouping is somewhat closer than in I(*b*), the δ-stereoisomeride.

We are at present investigating the action of heat on these semicarbazones, and also their behaviour towards aniline, which investigations we hope shortly to communicate to the Society. We are also extending this work to other semicarbazones derived from ketones and aldehydes.

EXPERIMENTAL.

The phenyl styryl ketone used in these experiments was prepared according to Claisen's method (*Ber.*, 1887, **20**, 657).

Phenyl Styryl Ketone Semicarbazones,
$CHPh\dot{:}CH\cdot CPh\dot{:}N\cdot NH\cdot CO\cdot NH_2$.

One molecular proportion of phenyl styryl ketone dissolved in the minimum quantity of alcohol was mixed with an aqueous-alcoholic solution of 2·5 molecular proportions of semicarbazide acetate obtained by treatment of semicarbazide hydrochloride (aqueous solution) with potassium acetate (alcoholic solution). The mixture was allowed to remain for forty-eight hours, when a white, crystalline mass was deposited, which consisted of the α-semicarbazone. On diluting the mother liquors with water and allowing to remain, yellow crystals of the β-modification, occasionally mixed with a small quantity of the α-form, were obtained. The yield of the β-modification varied very much, even under apparently similar conditions. Sometimes the α-modification alone was obtained; sometimes instead of the β-form an oil was precipitated, which could not be crystallised.

α-Modification.—The crude product was collected, washed with water, dried, and purified by precipitating the chloroform solution by addition of light petroleum. After a further recrystallisation from alcohol the semicarbazone was obtained in long, transparent needles, melting at 168° with slight decomposition. It is readily soluble in chloroform, hot alcohol, or carbon disulphide, forming colourless solutions, sparingly soluble in benzene and practically insoluble in water, ether, or light petroleum.

This α-modification is not affected by sunlight. An alcoholic solution of the semicarbazone when treated with sodium ethoxide becomes yellow, the depth of the colour increasing with the quantity of ethoxide added; the colour disappears on addition of acid. Attempts to isolate the yellow δ-modification from this solution were unsuccessful, the original α-semicarbazone always being regenerated. The absorption spectra of the α-semicarbazone in alcohol with and without sodium ethoxide are shown in Fig. 1:

0·1940 gave 26·4 c.c. N_2 at 18° and 758 mm. N = 16·0.
0·158 in 15·1 of chloroform gave E = 0·157°. M.W. = 244.
0·286 „ 15·1 „ „ E = 0·238°. M.W. = 291.
$C_{16}H_{15}ON_3$ requires N = 15·85 per cent. M.W. = 265.

These results indicate that the substance is unimolecular.

Hydrolysis of the α-Semicarbazone.—The semicarbazone was heated with 25 per cent. hydrochloric acid for about fifteen minutes. The yellow oil so obtained was extracted with ether, washed with water, dried, and the ethereal solution finally evaporated. The product was purified from a mixture of alcohol and light petroleum, and proved to be phenyl styryl ketone (m. p. 56—57°), the yield being almost theoretical.

From the results of hydrolysis and from the analysis, it is evident that this α-modification is undoubtedly a true semicarbazone of phenyl styryl ketone.

β-Modification.—Attempts to recrystallise this substance were unsuccessful, it being invariably converted into the colourless γ-modification. Attempts were made to recrystallise it from its own mother liquors, in which it is more stable, but by this means the substance could not be obtained in a state of purity.

γ-Modification.—This, as already mentioned, is obtained from the β-form by crystallisation, which was usually accomplished by dissolving in chloroform and adding light petroleum, the product being finally recrystallised from alcohol. This modification forms colourless needles melting at 179—180° with slight decomposition. In organic solvents the solubility of this γ-modification is similar to, but slightly greater than, that of the α-form. On exposure to light it rapidly becomes deep yellow, no change in weight taking place. That this action is solely due to light is proved by the fact that a specimen of the γ-stereoisomeride remains colourless if kept in the dark. This yellow form is apparently identical with the β-modification already described, since both on heating pass gradually into the γ-stereoisomeride at a temperature of about 170°. This identity is further supported by the fact that the yellow substance obtained by the action of light on the γ-modification, like the β-form, is converted by solvents into the γ-isomeride. Even moistening with a solvent such as chloroform is sufficient to bring about this change, no alteration in weight taking place; for example, 1·5352 grams of the γ-modification were exposed to light, when the yellow product weighed 1·5355 grams. After moistening with chloroform, which regenerated the γ-modification, and drying on the water-bath, the white product weighed 1·5347 grams.

Neutral solutions of the γ-modification are colourless. As in the case of the α-form, the alcoholic solution in the presence of sodium ethoxide is yellow, the colour being destroyed by acids. In this case, also, attempts to isolate a yellow substance from the alkaline solution resulted in failure, the γ-stereoisomeride being invariably recovered:

0·2126 gave 30·0 c.c. N_2 at 18° and 745 mm. N = 15·9.
0·1902, in 18·2 of chloroform, gave E = 0·157°. M.W. = 240.
0·3846, „ 18·2 „ „ E = 0·308°. M.W. = 252.
$C_{16}H_{15}ON_3$ requires N = 15·85 per cent. M.W. = 265.

Hydrolysis of the γ-Semicarbazone.—This was carried out exactly as described for the α-form, the product again being phenyl styryl ketone, which was obtained in almost theoretical amount.

Interconvertibility of the α- and γ-Modifications.

The first method tried was the action of heat on these modifications, but instead of stereoisomerides being produced this led to the formation of other products, which are at present under investigation.

The action of dry hydrogen chloride on the dry benzene solutions of these two modifications was next tried, and also the effect of boiling the chloroform solution of each with a small quantity of iodine; both of these methods, however, produced negative results.

Finally, it was found that the ultraviolet rays of a quartz-mercury lamp effected the mutual transformation of the isomerides.

Partial Transformation of the α- into the γ-Modification.

A solution of the α-isomeride in chloroform contained in a quartz flask was exposed to the light for varying periods of time, the distance of the solution from the lamp being about 10 cm. The most favourable results were obtained after an exposure of about fifteen hours. Light petroleum was then added to the solution, which caused the precipitation of the unchanged α-modification; by further addition of light petroleum to the mother liquors, the γ-form was obtained in approximately 30 per cent. yield. Further experiments to increase the amount of the γ-isomeride by longer exposure to ultraviolet light proved unsatisfactory owing to considerable resinification taking place.

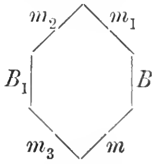
Partial Transformation of the γ- into the α-Modification.

This reaction was carried out as before, a 10 per cent. yield of the α-modification being obtained.

An equilibrium doubtless exists between the two isomerides, and would probably be realised by a longer exposure, but owing to resinification this could not be effected.

Dr. A. Hutchinson, M.A., kindly undertook the measurement of the crystals of the β- and γ-forms, an investigation rendered extremely difficult by the fact that small crystals only could be obtained. We abstract the following from his report:

"*β-Form.*—Flattened prisms, transverse section shown in figure. Angle from B and B_1 on to the adjacent m faces approximately 58°. Between crossed Nicols the crystals resting on B showed perfectly straight extinction, and gave polarisation colours of the fourth and fifth orders. Strong double refraction, refractive index of ray vibrating parallel to the length of the prism = 1·66, that of ray vibrating transversely = 1·75. The prisms exhibit remarkable pleochroism when viewed through B. Light vibrating transversely is strongly absorbed, the colour resulting being a fine greenish-yellow. On the other hand, light which vibrates parallel to the length of the prism suffers hardly any appreciable absorption, and when illuminated with polarised light vibrating in this direction the crystals remain almost colourless.



"No characteristic interference figure could be obtained in convergent light.

"The above observations render it probable that the substance crystallises in the ortho-rhombic system.

"*γ-Form.*—The general appearance, angles, indices of refraction, and optical orientation are identical with those of the β-form, the only difference observable being the absence of pleochroism. On exposure to light the yellow colour and pleochroism are developed."

We desire to record our thanks to Professor G. G. Henderson for the interest he has taken in this investigation.

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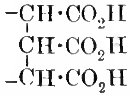
GLASGOW.

CLX.—*The Chemistry of the Aconitic Acids. Part I. The Labile Modification of Aconitic Acid and the Hydroxy-anhydro-acid.*

By NORMAN BLAND and JOCELYN FIELD THORPE.

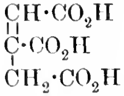
THE experiments published some years ago (Trans., 1906, **89**, 631) on the structure of aconitic acid led to the conclusion that this acid, like glutaconic acid, possessed a symmetrical structure, and that the same alkyl derivative was produced by the replacement of a hydrogen atom attached to either the α- or the γ-carbon atom.

It follows from the recent experiments on the structure of glutaconic acid (this vol., p. 871) that in all probability aconitic acid is represented by the normal structure (I),* but that if this is the case the labile form of the acid (II) must certainly be capable of isolation, because it has been shown that the presence of a substituting group on the central carbon atom of the three-carbon system confers stability on the labile forms of the acids of this type:



$$\begin{array}{l} -\mathrm{CH\cdot CO_2H} \\ \;\;| \\ \;\;\mathrm{CH\cdot CO_2H} \\ \;\;| \\ -\mathrm{CH\cdot CO_2H} \end{array}$$

Normal aconitic acid.
(I.)



$$\begin{array}{l} \mathrm{CH\cdot CO_2H} \\ \| \\ \mathrm{C\cdot CO_2H} \\ | \\ \mathrm{CH_2\cdot CO_2H} \end{array}$$

Labile aconitic acid.
(II.)

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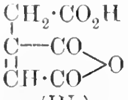
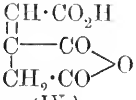
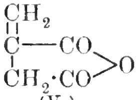
* It is probable that this formula represents the structure of the normal state with greater accuracy than that which places the tautomeric hydrogen atom in brackets (II), and in future the newer formula will be used.

The previous experiments with the glutaconic acids have shown that the labile modifications of the acids can always be isolated from the corresponding hydroxy-anhydrides by hydrating them in the presence of concentrated alkali or by dilute alkali in the presence of casein. It was therefore necessary to search for the hydroxy-anhydro-acid of aconitic acid in order to study its behaviour on hydration under similar conditions.

The dehydration of aconitic acid by acetyl chloride appears to have been first investigated by Easterfield and Sell (Trans., 1892, **61**, 1009), who isolated an anhydro-acid melting at 95°, to which they assigned the structure (III), because they considered it probable that the maleic type of anhydro-acid would be more easily produced than the succinic type:

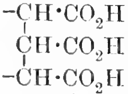

(III.)


(IV.)


(V.)

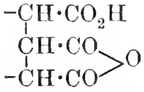
Subsequently Anschütz and Bertram (*Ber.*, 1904, **37**, 3967), using precisely the same conditions as those employed by Easterfield and Sell, isolated an anhydro-acid melting at 76°, to which they assigned the structure (IV) on account of the fact that it gave itaconic anhydride (V) when heated. These investigators regarded the melting point given by Easterfield and Sell as being due to a printer's error, but this supposition has neither been confirmed nor contradicted.

We experienced no difficulty in preparing considerable quantities of the anhydro-acid melting at 76° by treating the acid suspended in chloroform with acetyl chloride in accordance with the method of Anschütz and Bertram. The anhydro-acid gives no coloration with ferric chloride, and behaves on titration as a tribasic acid. It possesses, therefore, the normal anhydride structure, and is not the hydroxy-anhydro-acid. For reasons which will be given later, we consider that this anhydro-acid retains the normal structure of the acid, and that its formation can be represented in the following way:



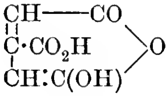
$$\begin{array}{l}-CH\cdot CO_2H\\ \;\;|\\ \;\;CH\cdot CO_2H\\ \;\;|\\ -CH\cdot CO_2H\end{array}$$

Acid.


Anhydride (m.p. 76°).

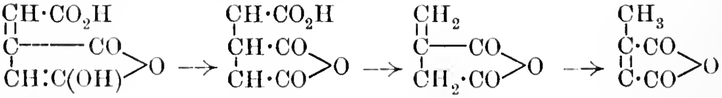
The search for the hydroxy-anhydro-acid among the residues from the preparation of the normal anhydro-acid were fruitless, and experiments with other dehydrating agents proved equally unsuccessful; ultimately the desired substance was prepared in the following way.

In a former paper (this vol., p. 857) we showed that Kahlbaum's pure acetyl chloride is without action on glutaconic acid, whereas his "acetylchlorid II" readily converts this acid into the hydroxy-anhydride. This difference in behaviour was ascribed to the presence of phosphorus trichloride in the commercial product, a substance which occurs only in traces in the pure reagent. The acetyl chloride used in the preparation of the anhydro-acid melting at 76° was the commercial product, which had been carefully fractionated. It still contained phosphorus trichloride, and, indeed, as Messrs. Kahlbaum kindly informed us, it is impossible to free it from this impurity by distillation unless the operation is carried out in the presence of glacial acetic acid. Acetyl chloride prepared in this way, as well as Kahlbaum's pure reagent, behaves towards aconitic acid in a manner markedly different from the impure reagent. At no stage during the reaction in chloroform does the acid pass into solution, but is gradually replaced by an insoluble, crystalline material, which when examined proved to be the desired hydroxy-anhydro-acid. The compound melts at 135°, and loses carbon dioxide a few degrees above this temperature; its hydroxy-structure is proved by its behaviour on titration, and by the production of an intense coloration with ferric chloride. It was at first thought that the structure of this substance was represented by formula VI, and a statement to this effect was made in the preliminary note recently published (Proc., 1912, **28**, 131), but so soon as larger quantities had been prepared it was evident that this view could not be upheld:



(VI.)

The compound is the hydroxy-form of the normal anhydro-acid, and is represented by formula VII. This is proved by the fact that when heated a degree or so above its melting point it is completely converted into the normal anhydro-acid (VII*a*); at a higher temperature carbon dioxide is eliminated, and itaconic anhydride (VIII) is produced, and finally on distillation citraconic anhydride (IX) is the sole product:



(VII.) M. p. 135°. (VII*a*.) M. p. 76°. (VIII.) (IX.)

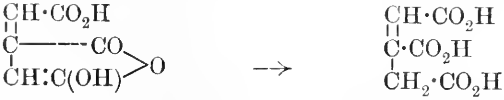
The statement made on a previous page that in our opinion the anhydro-acid melting at 76° retains the structure of the normal acid is based on a comparison of the two anhydro-acids in respect of their behaviour towards alkali. The hydroxy-anhydro-acid, both in water and in dilute alkali, forms yellow solutions, and the aqueous solution when rapidly titrated furnishes numbers corresponding with those required for a dibasic acid:

The normal anhydro-acid, on the other hand, dissolves in alkali, forming a colourless solution, and is hydrated to the salt of the tribasic acid without colour appearing at any stage during the operation; in fact, an aqueous solution of the anhydro-acid behaves on titration as a tribasic acid:

It is to be expected that if the two anhydro-acids were merely the tautomeric ketonic and enolic forms:

the conversion of the ketonic form into the salt of the enolic individual would be the first effect produced by the action of alkali. The proof is, of course, purely negative, and it is probable that no definite decision can be reached until a complete investigation of the esters of aconitic acid has been undertaken.

Having isolated the hydroxy-anhydro-acid we proceeded to study its behaviour on hydration with strong alkali and with dilute alkali in the presence of casein. We then found that whereas the normal anhydro-acid is completely converted into the known form of aconitic acid (m. p. 191°) under these conditions, the hydroxy-anhydro-acid yields an acid melting at 173°, which is evidently the labile form of aconitic acid formed in the following way:



Labile aconitic acid.

The labile acid is a comparatively stable substance, which differs from the normal acid in its behaviour towards acetyl chloride, since with both the impure and pure reagent it yields the hydroxy-anhydro-acid. It is slowly converted into the normal acid by boiling hydrochloric acid. The salts of the two modifications do not appear to show any points of difference.

Both normal and hydroxy-anhydro-acid yield the same anilino-acid with aniline:

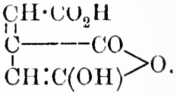
$$\begin{array}{l}\mathrm{CH\cdot CO_2H}\\ \|\\ \mathrm{C\text{------}CO}\\ |\\ \mathrm{CH{:}C(OH)}\end{array}\!\!>\mathrm{O} \longrightarrow \begin{array}{l}\mathrm{CH\cdot CO_2H}\\ \|\\ \mathrm{C\cdot CO_2H}\\ |\\ \mathrm{CH_2\cdot CO\cdot NHPh}\end{array}$$

but the substance prepared by us melts at 170°, whereas the melting point given by Bertram (*Ber.*, 1905, **38**, 1615) is 141°.* A direct comparison of the anilino-acids prepared from the two anhydro-acids showed them to be the same substance. Curiously enough, the same difficulty was experienced in identifying both itaconic and citraconic anhydrides by means of the semi-anilides; thus we found that the semianilide prepared from pure itaconic anhydride melted at 162° instead of 151·5°, and the semianilide from citraconic anhydride at 175° instead of 153°, the temperatures recorded in the literature.

It must be remembered, however, that all these compounds decompose at or immediately above their melting points, and that, therefore, the melting point is probably influenced by the manner of heating. The melting points recorded by us were taken in the bulb form of apparatus, and the sulphuric acid was rapidly heated to within a few degrees of the observed melting point.

EXPERIMENTAL.

The Hydroxy-anhydro-acid of Aconitic Acid (2-*Hydroxy*-5-*keto*-2:5-*dihydrofurfurylidene*-4-*acetic Acid*),



$$\begin{array}{l}\mathrm{CH\cdot CO_2H}\\ \|\\ \mathrm{C\text{------}CO}\\ |\\ \mathrm{CH{:}C(OH)}\end{array}\!\!>\mathrm{O}.$$

The most convenient method for the preparation of this substance was found to be as follows: Forty grams of finely ground aconitic acid are mixed with a solution of 80 grams of pure acetyl chloride (acetylchlorid "Kahlbaum") in 200 grams of absolute chloroform, and heated to the boiling point for eight hours. At the end of this time an examination of the undissolved material with the aid of a lens showed that the ill-defined crystals of aconitic acid had been replaced by the clearly defined needles of the hydroxy-anhydro-acid; it is quite easy by this means to determine the end-point of the reaction. The insoluble material was then collected, washed with chloroform, and dried on a porous plate; it melted sharply at 135°, evolving gas a few degrees above this temperature. For

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* A private communication from Prof. Anschütz informs us that this number is a misprint for 171°.

the purposes of analysis it was recrystallised from ethyl acetate, from which it separated in short, slender needles of the same melting point as that given above:

0·1558 gave 0·2660 CO_2 and 0·0386 H_2O. C=46·47; H=2·75.
0·1902 „ 0·3210 CO_2 „ 0·0448 H_2O. C=46·03; H=2·62.
$C_6H_4O_5$ requires C=46·2; H=2·6 per cent.

The hydroxy-anhydro-acid is sparingly soluble in all the usual organic solvents. It forms a greenish-yellow solution in water, to which ferric chloride imparts a deep reddish-brown coloration. It dissolves in aqueous alkaline carbonates, forming yellow solution, from which the colour slowly disappears on keeping. When the aqueous solution is rapidly titrated, figures are obtained corresponding with those required for the dibasic acid:

0·3324 required 22·0 c.c. NaOH solution (1 c.c.=0·00785 gram NaOH).
$C_6H_4O_5$ (dibasic) requires 21·7 c.c.

The hydration of the hydroxy-anhydro-acid in aqueous solution is, however, fairly rapid, and higher figures than these are obtained if the solution is kept.

The amount of the hydroxy-anhydro-acid prepared in this manner was 15 grams, that is, about 45 per cent. of the theoretical amount from the quantity of aconitic acid used. The residue remains as a viscid mass when the excess of chloroform and acetyl chloride is evaporated in a desiccator over potassium hydroxide. Practically the whole of this material is extracted by boiling benzene, and separates from the cooled solution as the characteristic flattened needles (resembling phthalic anhydride) of the Anschütz and Bertram anhydro-acid, melting at 76°. We could find no trace of an anhydro-acid melting at 95° corresponding with that prepared by Easterfield and Sell. It is possible that this substance may have the glutaconic structure (formula VI, p. 1492), formed by conditions not easily reproduced, and it would therefore be of interest to know if this melting point is a misprint, as suggested by Anschütz and Bertram.

The Conversion of the Hydroxy-anhydro-acid into the Normal Anhydro-acid.

Three grams of the hydroxy-anhydro-acid were heated in a bath of sulphuric acid at 140°, the temperature being carefully regulated so as to prevent the evolution of carbon dioxide. At the end of ten minutes the product was cooled and extracted with hot benzene, when the solvent on cooling deposited the characteristic needles of the normal anhydro-acid melting at 76°. (Found, C=46·09:

$H=2\cdot63$. Calc., $C=46\cdot2$; $H=2\cdot6$ per cent.) For the sake of comparison with the hydroxy-anhydro-acid, this substance was titrated, when figures were obtained corresponding with those required for a tribasic acid:

0·2200 required 20·95 c.c. of NaOH solution (1 c.c.=0·00785 gram NaOH).

$C_6H_4O_5$ (tribasic) requires 21·6 c.c.

The figures show that the anhydro-acid was not completely converted into the tribasic acid. By adding excess of alkali and titrating back, 21·5 c.c. of the alkali were required.

The Formation of Itaconic and Citraconic Anhydrides.—Three grams of the hydroxy-anhydro-acid were heated at 170° until the evolution of carbon dioxide had ceased, when the cooled residue was rubbed with dry ether and the solid material collected. It melted at 68°, and was identified as itaconic anhydride by direct comparison with a specimen of this compound prepared from itaconic acid. (Found, $C=53\cdot42$; $H=3\cdot61$. Calc., $C=53\cdot6$; $H=3\cdot6$ per cent.)

Ten grams of the hydroxy-anhydro-acid were distilled at the ordinary temperature; some charring occurred, but the major portion distilled at 213° as a liquid, which solidified when cooled in ice and salt, and then melted at 7°. (Found, $C=53\cdot51$; $H=3\cdot63$. Calc., $C=53\cdot6$; $H=3\cdot6$ per cent.)

Both anhydrides were identified by means of their semianilides, which are readily prepared in dry ethereal solution. Some little difficulty was at first experienced, owing to the high melting points of the semianilides obtained from our products. Ultimately a direct comparison with the semianilides obtained from itaconic and citraconic anhydrides prepared from the pure acids showed that when taken in the ordinary bulb form of apparatus the melting points of these substances are considerably higher than those recorded in the literature; thus the semianilide of itaconic acid was found to melt at 162° with elimination of water-vapour at 175°. (Found, $C=64\cdot53$; $H=5\cdot02$. Calc., $C=64\cdot7$; $H=4\cdot9$ per cent.), whereas the semianilide of citraconic acid was found to melt with immediate decomposition at 175°. (Found, $C=64\cdot61$; $H=5\cdot06$. Calc., $C=64\cdot7$; $H=4\cdot9$ per cent.)

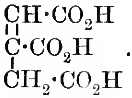
The Anilino-acid from the Hydroxy-anhydro-acid.—It is mentioned in the introduction that the same anilino-acid is formed from the hydroxy-anhydro-acid as from the normal anhydro-acid, but it was some time before this fact could be established owing to the low melting point (141°) given by Bertram (*Ber.*, 1905, **38**, 1615) for this substance. It was therefore necessary to prepare the anilino-acid from both anhydro-acids, and to compare them. The anilino-acid from the hydroxy-anhydro-acid can be prepared by adding rather more than the calculated amount (1 molecule) of aniline dissolved in ethyl acetate to a solution of the anhydride in the same solvent. It separates as a viscid mass, which adheres to the walls of the containing vessel, and can be removed from the solvent by decantation. It can be obtained solid and free from admixed aniline salt by rubbing with dilute hydrochloric acid, and can be isolated in small, pale yellow prisms from alcohol. It melts at 170° with immediate evolution of gas, and does not give the red colour with aqueous alkali hydroxide, as stated by Bertram, although the alcoholic mother liquor from the recrystallisation was found to give this reaction:

0·1177 gave 0·2492 CO_2 and 0·0470 H_2O. C=57·73; H=4·44.

$C_{12}H_{11}O_5N$ requires C=57·8; H=4·4 per cent.

The anilino-acid from the normal anhydro-acid was prepared by Bertram's method in ethereal solution. It is probable that his product contained traces of the aniline salt of the anilino-acid, because although we adhered strictly to his conditions we were unable to obtain the product in a pure condition without first treating it with dilute hydrochloric acid. The anilino-acid prepared in this manner had precisely the same properties as those given for the substance described above. Both products yield citraconanil (m. p. 98°) when heated.

Labile Aconitic Acid,



$$\begin{array}{l} CH\cdot CO_2H \\ \| \\ C\cdot CO_2H \\ | \\ CH_2\cdot CO_2H \end{array} .$$

This acid may be obtained in quantity from the hydroxy-anhydro-acid by the following process: Five grams of the anhydride are dissolved in 30 c.c. of a 30 per cent. aqueous solution of potassium hydroxide, and kept at the ordinary temperature until the yellow colour of the solution has disappeared. An equal volume of water is then added and sufficient hydrochloric acid to effect complete neutrality, the solution being kept cold throughout the process. After being evaporated to a small bulk on the water-bath, the residue is mixed with the calculated amount of hydrochloric acid to convert the sodium salt of the tribasic acid into the free acid, and is then extracted several times with ether. On evaporating the dried ethereal solution to a small bulk, the acid separates as a crystalline powder, and can be purified by washing with pure ether. It melts at 173°, evolving gas at a few degrees above this temperature:

0·2139 gave 0·3231 CO_2 and 0·0668 H_2O. C=41·19; H=3·47.

$C_6H_6O_6$ requires C=41·4; H=3·4 per cent.

The acid prepared in this manner closely resembles normal aconitic acid in appearance. It is readily soluble in water, and can be obtained as well-defined, slender needles by the slow evaporation of its aqueous solution. It exhibits no points of difference from normal aconitic acid in respect of its salts, but differs markedly from this acid in its behaviour on dehydration, since with both pure acetyl chloride, as well as with this reagent containing phosphorus trichloride, it is completely converted into the hydroxy-anhydro-acid. The labile acid behaves in the same manner as the normal acid when heated above its melting point, since, as already shown, the hydroxy-anhydro-acid is converted into the anhydro-acid at 140°.

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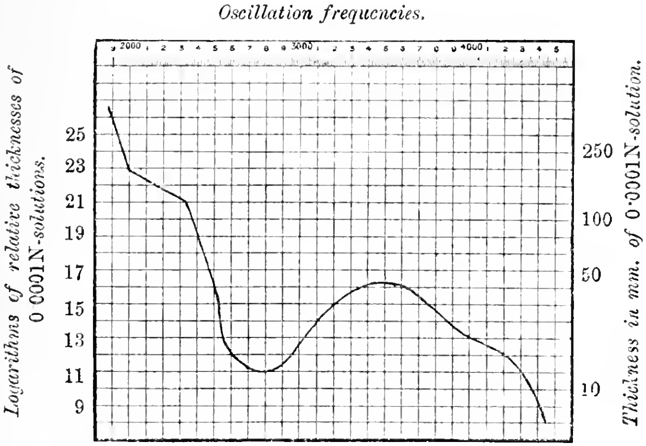
CLXI.—*Substituted Thiolazo-derivatives of Benzene.*

By JOHN JACOB FOX and FRANK GEORGE POPE.

ALTHOUGH phenyl mercaptan resembles phenol in its general characters, it has hitherto not been found possible to couple it directly with diazonium salts so as to yield thiol derivatives corresponding with benzeneazophenol. Hantzsch and Freese (*Ber.*, 1895, **28**, 3241) found that benzenediazonium chloride and an alkaline solution of phenyl mercaptan yielded an unworkable oil, whilst with other diazonium salts diazothiophenyl ethers resulted, having the constitution R·N:N·SPh. These substances are readily decomposed with hydrochloric and sulphuric acids, have low melting points, and are more nearly related to diazoamino-compounds than to benzeneazophenol. It seemed possible that thiolazo-derivatives might be obtained through the xanthic esters by the method described by Leuckart (*J. pr. Chem.*, 1890, [ii], **42**, 187). Aminoazobenzene was used by Leuckart, but he finally obtained a disulphide, $(C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}S)_2$, after hydrolysis of the xanthic ester by alcoholic potassium hydroxide. Whilst it was not found possible to isolate benzeneazophenyl mercaptan in a pure state by acidification of the alkaline solution resulting from this hydrolysis, we were able to obtain the methyl and ethyl ethers of benzeneazophenyl mercaptan by treatment of the potassium salt with the corresponding alkyl iodides. The methyl and ethyl ethers of benzeneazophenyl mercaptan are stable solids resembling the ethers of benzeneazophenol. The course of the reaction whereby these substances are obtained is shown by the following scheme:

$$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2 \longrightarrow C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}S{\cdot}C_3H_5OS \longrightarrow$$
$$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}SK \longrightarrow C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}S{\cdot}CH_3.$$

They are in all respects strictly analogous to the latter substances, that is, they give hydrochlorides, platinum salts, and combine with water, giving substances of the type $(Ph{\cdot}N_2{\cdot}C_6H_4S{\cdot}R)_2,H_2O$. The curve for the absorption spectrum is of the same type as was found by Tuck for benzeneazophenetole (Trans., 1907, **91**, 449) and by Hewitt and Thomas for aminoazobenzene (Trans., 1909, **95**, 1295). It is noteworthy that the curve occupies an intermediate position between that of benzeneazophenetole and of aminoazobenzene. The positions of the heads of the bands are as follows:



Benzeneazothioanisole in alcohol.

$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}OEt$	about $1/\lambda$	2900
$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}SMe$	,, ,,	2740
$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2$	,, ,,	2600

The solutions of the thiolazo-compounds in strong mineral acids are purple as compared with yellowish-brown of benzeneazophenol and yellow of aminoazobenzene.

p-Nitrobenzeneazophenylmethylmercaptole was prepared in small amount by the coupling of *p*-nitrobenzenediazonium chloride with an alkaline solution of phenyl mercaptan and treatment of the potassium salt of the resulting *p*-nitrobenzeneazophenyl mercaptan with methyl iodide, the main product of the reaction, however, consisting of *p*-nitrodiazobenzenethiophenyl ether.

EXPERIMENTAL.

Benzeneazophenylmethylmercaptole.—19·7 Grams of aminoazobenzene were made into a paste with 22 grams of hydrochloric acid (D 1·17: or the equivalent proportion of sulphuric acid) and 100 c.c. of water. The salt was diazotised with 6·9 grams of sodium nitrite, and allowed to remain in ice-water until practically all the original suspended matter was dissolved. The resulting diazonium solution was filtered, and added a little at a time to a moderately strong solution of 17 grams of potassium xanthate in water at a temperature of about 75°. Each addition of diazonium salt was followed by a violent evolution of gas and the separation of a red oil. When all the diazonium solution had been added, the vessel was warmed on a water-bath for half an hour and then cooled. The aqueous liquid was decanted from the xanthic ester, which was dissolved in benzene and treated successively with a little hydrochloric acid and aqueous sodium hydroxide to remove any aminoazobenzene or benzeneazophenol. The benzene was removed by evaporation, leaving the xanthic ester practically pure, as described by Leuckart (*loc. cit.*). Without further purification the xanthic ester was dissolved in an excess of 8 per cent. alcoholic potassium hydroxide, and boiled for twenty hours under a reflux condenser. The deep magenta-coloured liquid was then decanted from a little tarry matter and mixed with excess of methyl iodide, and heated under a reflux condenser until the liquid was almost neutral. The alcoholic solution was diluted with water, the precipitated yellow solid collected, washed with water, and recrystallised from 60 per cent. alcohol or 90 per cent. acetic acid. From both these solvents benzeneazophenylmethylmercaptole crystallises in hard, orange-coloured needles, melting at 83—84°. The yield of pure product is from 4 to 5 grams from 20 grams of aminoazobenzene.

Benzeneazophenylmethylmercaptole dissolves readily in the usual organic solvents, and is best crystallised from dilute acetic acid. It is insoluble in alkali hydroxides, and dissolves in concentrated sulphuric acid with a deep purple colour:

0·1606 gave 0·4022 CO_2 and 0·0774 H_2O. C = 68·3; H = 5·4.
0·1478 „ 15·6 c.c. N_2 at 17° and 756 mm. N = 12·3.
0·2744 „ 0·2772 $BaSO_4$. S = 13·9.
$C_{13}H_{12}N_2S$ requires C = 68·4; H = 5·3; N = 12·3; S = 14·0 per cent.

Attempts to obtain benzeneazophenyl mercaptan in the free state were not altogether successful. If the alkaline solution obtained after hydrolysis of the xanthic ester is acidified, an orange-coloured precipitate of the thiolazo-derivative results, but this is oxidised to disulphide on removal from the liquid. Operating in an atmosphere of carbon dioxide was more successful, but the dry product after crystallisation from alcohol was only partly soluble in aqueous sodium hydroxide, owing to rapid oxidation, and did not possess a sharp melting point, although the portion which actually dissolved in the sodium hydroxide yielded a deep magenta-coloured solution.

The absorption spectrum of benzeneazophenylmethylmercaptole is of particular interest, inasmuch as the type of curve obtained is similar in character to that of benzeneazophenol, including the "step-out," obtained with solutions of the latter, using the nickel-iron spark. The head of the band for benzeneazophenylmethylmercaptole is nearer the red end of the spectrum than the band of benzeneazophenol (or benzeneazophenetole), and the curve slopes towards the red rather rapidly with increasing concentration of the solution.

Benzeneazophenylmethylmercaptole Hydrochloride.—Through a solution of benzeneazophenylmethylmercaptole in benzene dry hydrogen chloride is passed so long as any precipitate forms. The flocculent precipitate is collected, and rapidly dried on a porous tile. The hydrochloride so obtained is a reddish-brown powder with a metallic glance, and is unstable in moist air. It decomposes on heating a little above 100°:

0·1886 gave 0 1072 AgCl. Cl = 14·0.
$C_{13}H_{12}N_2S,HCl$ requires Cl = 13·4 per cent.

On exposure to moist air the hydrogen chloride is replaced by water, and at the same time the substance becomes paler in colour. The hydrate so formed has the composition $(C_{13}H_{12}N_2S)_2,H_2O$, and retains the water somewhat persistently on drying:

0·1192 gave 0·2868 CO_2 and 0·0616 H_2O. C = 65·6; H = 5·7.
$C_{13}H_{12}N_2S,\frac{1}{2}H_2O$ requires C = 65·8; H = 5·5 per cent.

Additive products with methyl iodide were not obtained, a large proportion of the original substance being recovered on heating benzeneazophenylmethylmercaptole under pressure with methyl iodide and methyl alcohol

Benzeneazophenylmethylmercaptole Platinichloride.—This substance was prepared by dissolving benzeneazophenylmethylmercaptole in glacial acetic acid, adding platinic chloride, and passing dry hydrogen chloride into the solution. It separates as a violet powder:

0·2262 gave 0·0334 Pt. Pt = 14·8.
$(C_{13}H_{12}N_2S)_4,H_2PtCl_6$ requires Pt = 14·8 per cent.

When obtained by evaporation of a strongly acid alcoholic solution, the salt approximates in composition to $(C_{13}H_{12}N_2S)_2,H_2PtCl_6$. (Found, Pt = 19·9. Calc., Pt = 22·7 per cent.)

Benzeneazophenylethylmercaptole.—This substance was prepared in a similar manner to the methyl derivative described above, except that ethyl iodide was used in the place of methyl iodide. The product was yellower than the methyl derivative, but behaved similarly and melted at 72°:

0·1240 gave 0·3172 CO_2 and 0·0676 H_2O. C = 69·8; H = 6·1.
0·1446 „ 14·7 c.c. N_2 at 18° and 747 mm. N = 11·8.
0·2336 „ 0·2214 $BaSO_4$. S = 13·0.
$C_{14}H_{14}N_2S$ requires C = 69·4; H = 5·8; N = 11·6; S = 13·2 per cent.

Benzeneazophenylethylmercaptole Hydrochloride.—This was prepared from a solution of benzeneazophenylmethylmercaptole in benzene; it decomposed below 100°. (Found, Cl = 12·9. $C_{14}H_{14}N_2S,HCl$ requires Cl = 12·7 per cent.)

The *hydrate* obtained from the hydrochloride by means of moist air corresponded in composition with $C_{14}H_{14}N_2S,\frac{1}{2}H_2O$. (Found, H_2O = 3·4. Calc., H_2O = 3·6 per cent.)

It has been shown by Hantzsch and Freese (*Ber.*, 1895, **28**, 3241) that the coupling of diazonium solutions with phenyl mercaptan does not produce substances analogous to benzeneazophenol. Working, however, with larger quantities of materials we were able to obtain the methyl ether of *p*-nitrobenzeneazophenyl mercaptan. 13·8 Grams of *p*-nitroaniline were diazotised, and the solution was poured into an alkaline solution of 11 grams of phenyl mercaptan kept near 0°. An immediate separation of a dark yellow solid resulted, and this increased on keeping. After twenty-four hours the yellow solid was collected, washed, and recrystallised from alcohol. This substance, which is the main product of the reaction, was *p*-nitrodiazobenzenethiophenyl ether, melting at 96°, and agreed in properties with the compound described by Hantzsch and Freese. The clear alkaline filtrate from this substance was of greenish colour, and was saturated with carbon dioxide and boiled in an atmosphere of carbon dioxide to remove unchanged phenyl mercaptan. A brown solid separated, which was collected and washed in carbon dioxide. This solid is probably *p*-nitrobenzeneazophenyl mercaptan. It was dissolved in alcoholic potassium hydroxide, and boiled under a reflux condenser with an excess of methyl iodide, as in the preparation of benzeneazophenylmethylmercaptole. The alcoholic solution was treated as in the latter case, and the brown solid was crystallised from 85 per cent. acetic acid. It crystallised in small needles melting at 137°:

0·1548 gave 20·5 c.c. N_2 at 20° and 750 mm. N = 15·2.
0·3038 „ 0·2532 $BaSO_4$. S = 11·5.
$C_{13}H_{11}O_2N_3S$ requires N = 15·4; S = 11·7 per cent.

p-*Nitrobenzeneazophenylmethylmercaptole* is moderately soluble in alcohol, benzene, or chloroform, and readily so in glacial acetic acid. It yields a reddish-brown solution in concentrated sulphuric acid, and does not decompose with strong acid, as in the case of *p*-nitrodiazobenzenethiophenyl ether.

We desire to express our thanks to the Research Fund Committee of the East London College for a grant towards the cost of this investigation.

EAST LONDON COLLEGE.

CLXII.—*The Conditions of Isodynamic Change in the Aliphatic Ketones. Part I. The Autocatalytic Reaction between Acetone and Iodine.*

By HARRY MEDFORTH DAWSON and FRANK POWIS, M.Sc.

IT has been shown in a previous communication (Dawson and Leslie, Trans., 1909, **95**, 1864) that iodine slowly disappears when added to a neutral aqueous solution of acetone, and that the rate of disappearance increases rapidly as the reaction proceeds in consequence of the formation of hydrogen iodide, which acts as a catalyst in connexion with the primary tautomeric change of the ketone. The further investigation of this autocatalytic reaction appeared to be of considerable interest in view of the possibility that some light would be thrown on the conditions which determine or preclude, accelerate or retard, the keto ⟶ enol transformation. The experimental work described in this paper was carried out with this object in view.

From a series of measurements, in which small quantities of hydrogen chloride (0·005 to 0·05 mol. per litre) were added to the acetone solution, it has been found that the rate of disappearance of iodine is almost exactly proportional to the concentration of the acid. Above this range of acidity, this proportionality is no longer evident, the ratio of the velocity of the reaction to the acid concentration increasing with the quantity of halogen acid present. From the observed relationship between the two quantities, it seems probable, however, that the velocity will be exactly proportional to the concentration of the halogen acid in very dilute acid solutions.

At the outset, attention may be directed to a difference between the auto-accelerated change and the constant speed reaction which occurs in presence of excess of acetone and of a sufficient quantity of a mineral acid catalyst. In the latter case, if the speed of the reaction is measured by the rate of disappearance of iodine from the solution, two stages are involved, as represented by the formulæ (1) and (2):

$$CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_2{:}C(OH){\cdot}CH_3 \qquad (1)$$

$$CH_2{:}C(OH){\cdot}CH_3 + I_2 \longrightarrow CH_2I{\cdot}CI(OH){\cdot}CH_3 \qquad (2)$$

but in the case of the auto-accelerated change the speed of the relatively very slow isomeric change (1) is obviously determined by a third reaction, which gives rise to the halogen acid catalyst, namely, that represented by

$$CH_2I{\cdot}CI(OH){\cdot}CH_3 \longrightarrow CH_2I{\cdot}CO{\cdot}CH_3 + HI \qquad (3)$$

If the velocity of the third reaction, like that of the second, is relatively very large, it is evident that the quantity of acid which has been formed after a given time interval may be determined by measurement of the fall in the iodine concentration, and that the rate of progress of the slow primary change at any moment will be dependent on the extent to which the third reaction has taken place.

If x represents the concentration of the hydrogen iodide which has been set free after time t in an originally "neutral" aqueous solution containing c molecules of acetone per litre and a relatively small quantity of iodine, then the velocity at this moment should be given by:

$$dx/dt = k \, . \, c \, . \, x \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where k denotes the velocity of isomeric change in a solution containing 1 molecule of acetone per litre and 1 molecule of halogen acid per litre. The integrated form of this equation:

$$lnx = kct + C,$$

in which C is a constant, is in very satisfactory agreement with the actual measurements of the progress of the auto-accelerated change over the period covered by the determinations of the changes in the iodine concentration. By extrapolation of the straight line which is obtained by plotting lnx as a function of t, it is found, however, that the initial speed of the reaction is much greater than can be accounted for on the basis of the acidity of the original "neutral" solution.

In reference to this high initial velocity, it may be mentioned that conductivity water was in all cases used in the preparation of the solutions. The specific conductivity of this varied from 1 to 2×10^{-6} mho., whereas the initial speed, indicated by the above method of extrapolation, would correspond with a conductivity of about 8×10^{-6} mho., if it is assumed that the reaction is conditioned by the presence of an acid catalyst. It is improbable that the acidity of the solvent is influenced to any appreciable extent by the dissolved acetone or the potassium iodide which was added to increase the solubility of the iodine and diminish its volatility. On the other hand, the iodine may have a measurable influence on the acidity, for according to Bray (*J. Amer. Chem. Soc.*, 1910, **32**, 932) the conductivity of a saturated aqueous solution of iodine at 25° is about 4×10^{-6} mho. This conductivity increases slowly to a considerably higher value, but the rate of increase is such that it cannot be supposed to affect the initial speed of the reaction with which we are concerned. The conductivity 4×10^{-6} mho. is attributed to the hydriodic acid which results from the hydrolysis $I_2 + H_2O \rightleftharpoons H^{\cdot} + I' + HIO$. In presence of potassium iodide the degree of hydrolysis must be much smaller than in a pure aqueous solution of iodine, and since potassium iodide was always added to our solutions, usually in the ratio $2KI : I_2$, it is not possible to account for the initial rate of change on the basis of the acidity of the solvent, of the dissolved substances, or of the substances formed by the interaction of these with the solvent.

In a further attempt to account for the high initial velocity, it was thought that this might be due to the small proportion of the enolic isomeride which is present in the acetone in equilibrium with the predominant ketonic form. In consequence of the rapid interaction between the enol and the iodine, it is conceivable that hydriodic acid might be formed according to equation (3) in sufficient quantity to start the reaction at a speed corresponding with the extrapolated halogen acid concentration.

In order to test this hypothesis, a dilute solution of iodine of known concentration was made up to twice its volume by addition of an aqueous acetone solution, and the concentration of the iodine in the resulting mixture was determined. The titration numbers showed that if any iodine had disappeared, the quantity was smaller than could be recognised by this method of observation.

A more sensitive method was then adopted. This consisted in comparing the electrical conductivity of iodide-free iodine and acetone solutions with that of the solution obtained by mixing these in known proportions. If it is assumed that the third stage in the reaction takes place with considerable speed, an assumption which would appear to be justified by the general results obtained in the dynamic investigation of the autocatalytic change, it is evident that any enolic acetone present would give rise immediately to an equimolecular quantity of hydriodic acid, which even in very small quantities should be indicated by the electrical conductivity measurements. The actual observations made according to this method seem to show a very slight rise in the electrical conductivity when the iodine and acetone solutions are mixed, but this increase is quite inadequate to account for the initial rate of isomeric change in the originally "neutral" solution.

The question therefore arises as to whether the initial speed as obtained by extrapolation may not be due, at any rate in part, (1) to the natural velocity of the reaction

$$CH_3{\cdot}CO{\cdot}CH_3 \rightarrow CH_2{:}C(OH){\cdot}CH_3,$$

that is, to the progress of the uncatalysed reaction, or (2) to the action of other than acid catalysts which may be conveniently referred to under the head of non-acid catalysts. The consideration of this question may be deferred until the experimental observations have been recorded.

Whatever the cause of the initial effect, it is evident that this may be very conveniently expressed in terms of halogen acid concentration. Representing it by x_0 (mols. halogen acid per litre), then in reference to equation (1) we have $x = x_0$ when $t = 0$. As will be seen later, the initial non-acid influence, represented by x_0, appears to diminish when very small quantities of halogen acid are added to the solution at the commencement of the reaction, and when the autocatalysis in the originally "neutral" solution has proceeded so far as to allow of accurate measurements of x, the initial (catalytic) effect, instead of remaining constant throughout the reaction, has probably been more or less completely eliminated. Taking this into account, integration of (1) leads to the equation:

$$k = \frac{1}{ct} \ln \frac{x}{x_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The experimental data obtained in the autocatalytic experiments will now be considered in reference to this equation. The measurements were carried out at 25°, conductivity water, redistilled "bisulphite" acetone, and carefully purified iodine and potassium iodide being used in the preparation of the solutions which were contained in well-steamed, stoppered flasks. After suitable time intervals, a measured volume of solution was removed, added to an excess of sodium acetate solution, and the iodine titrated with freshly prepared $0{\cdot}01N$-sodium thiosulphate.

Tables I to III contain the data obtained in experiments with aqueous solutions of acetone to which only iodine and potassium iodide were added. The first three columns give respectively the time in hours, the iodine concentration, and the halogen acid concentration (x) in mols. per litre, the latter being assumed to be equivalent to the iodine which has disappeared; the fourth column shows the calculated values of $k=\frac{1}{ct}ln\frac{x}{x_0}$. In order to obtain the value of x_0, k was first calculated from the data for the middle and later stages of the reaction by means of the modified equation $k=\frac{1}{c(t_2-t_1)}.ln\frac{x_2}{x_1}$ in which x_1 and x_2 are the values of x corresponding with the time intervals t_1 and t_2. The measure of the effect which determines the apparent initial speed of the reaction is then obtained by inserting this k value in the equation $x_0=x.e^{-kct}$. Corresponding with the series of t values for a particular experiment, a series of values of x_0 can be obtained, and the mean of these has been employed in calculating the values of k which are tabulated.

TABLE I.

Acetone, 20 c.c. per litre. Iodine, 0·004 molar. KI, 0·008 molar. Solvent, $\kappa=1·5\times10^{-6}$ mho. $x_0=0·000023$.

Time (hours).	Mols. I_2 per litre.	x.	$k=\frac{1}{ct}.ln\frac{x}{0·000023}$.
0	0·003976	0	—
72	0·003814	0·000162	0·100
115	0·003385	0·000591	0·1035
140	0·002758	0·001218	0·104
163	0·001616	0·002360	0·1045
170	0·001110	0·002866	0·104
174	0·000814	0·003162	0·104

TABLE II.

Acetone, 20 c.c. per litre. Iodine, 0·004 molar. KI, 0·008 molar. Solvent, $\kappa=2·0\times10^{-6}$ mho. $x_0=0·000021$.

0	0·003984	0	—
100·5	0·003608	0·000372	0·105
126	0·003221	0·000763	0·1045
149	0·002540	0·001444	0·1045
168	0·001512	0·002472	0·1045

TABLE III.

Acetone, 20 c.c. per litre. Iodine, 0·005 molar. KI, 0·01 molar. Solvent, $\kappa=1·0\times10^{-6}$. $x_0=0·000019$.

0	0·004992	—	—
76	0·004862	0·000130	0·093
99·3	0·004701	0·000291	0·101
123·1	0·004392	0·000600	0·103
143·9	0·003902	0·001090	0·1035
170·8	0·002676	0·002316	0·1035
191·2	0·000915	0·004077	0·103

The constancy of the series of values of k in each table indicates that the progress of the autocatalytic change is quite satisfactorily represented by means of equation (2) so far as the period covered by the experimental observations is concerned. On account of the considerable errors which would necessarily attach to the estimation of the change in the iodine concentration, no measurements are possible until two or three days have elapsed, and for this reason the calculated value of x_0 is of particular interest, inasmuch as it indicates what the initial speed of the reaction would have to be to account for the observed course of the change, if it were assumed that the nature of the reaction in its earliest stages is the same as that during the experimental period.

In other experiments, carried out under essentially the same conditions as those which obtained in the examples which have been recorded in detail, a similar degree of constancy of the separate values of k was found. The mean value of k from all the experiments, in which no sensible fluctuation of temperature was observed, is 0·1035, and that of x_0 0·000021.

Whether specially purified conductivity water of low conductivity or ordinary distilled water was used in the preparation of the solutions does not appear to have any marked influence on the extrapolated value of x_0, and the employment of different preparations of acetone, iodine, and potassium iodide was also found to have no appreciable effect on the apparent initial speed of the reaction. Variation in the concentration of the iodine and of the ratio of potassium iodide to iodine also appears to be without influence on the value of x_0.

If, however, very small quantities of halogen acid are added to the original solution and allowance is made for this, smaller values are obtained for x_0. Denoting the concentration of the added halogen acid by a, and the extrapolated initial acid concentration by $a + x_0$, then the values obtained for x_0 in this way are found to decrease as the concentration of the added acid increases. In table IV are recorded the data which were obtained in such an experiment.

TABLE IV.

Solution as in experiment 1, with the addition of HCl to give a 0·000020 molar solution. $a + x_0 = 0·000034$. $x_0 = 0·000014$.

Time (hours).	Mols. I_2 per litre.	x.	$k = \frac{1}{ct} \ln \frac{x}{a + x_0}$.
0	0·003979	0·000020	—
51	0·003883	0·000116	0·088
72	0·003757	0·000242	0·100
96	0·003506	0·000493	0·102
118	0·003080	0·000919	0·1025
129	0·002730	0·001269	0·103
148	0·001853	0·002146	0·103
167	0·000377	0·003622	0·103

In other similar experiments, larger quantities of halogen acid were added at the outset. The detailed record of these experiments is unnecessary, the data tabulated in the following summary showing clearly enough the nature of the results:

TABLE V.

Concentration of added halogen acid.	x_0.
0	0·000021
0·000020	0·000014
0·000020	0·000013
0·000040	0·000009
0·000080	0·000004

From the fact that x_0 diminishes as the quantity of halogen acid added to the original solution increases, it would seem that the initial speed in "neutral" solution is due to some substance or substances, the activity of which is gradually depressed by the addition of halogen acid. This result is opposed to the view that the initial effect in "neutral" solution is due to the natural velocity of the keto $\longrightarrow$ enol transformation, and shows rather that the reaction in the initial stages proceeds under the influence of some substance which may act as a base.

In a further attempt to elucidate the nature of the initial stages, experiments were made in which small quantities of sodium hydroxide were added to the solution of the reacting substances. There can be little doubt that the added alkali reacts at once with the iodine to form hypoiodite and iodide, and according to Schwicker's measurements (*Zeitsch. physikal. Chem.*, 1895, **16**, 303) of the rate of decomposition of aqueous solutions of potassium hypoiodite, it may be inferred that the resulting hypoiodite is rapidly decomposed. The initial estimation of the concentration of the iodine indicates, in fact, that a quantity of iodine has disappeared which corresponds approximately with the formation of hypoiodite, and if this is then decomposed in a comparatively short time with the formation of iodide and iodate, the only effect of the addition of alkali hydroxide will be to neutralise the traces of acid impurities which may be present in the solution. It can have no appreciable influence on the acidity resulting from the hydrolysis of the iodine. As a matter of fact, the observed progress of the change in such solutions differs comparatively little from that in the "neutral" solutions of tables I—III, as is evident from the following data:

TABLE VI.

Solution as in experiment 1, with the addition of sodium hydroxide to give a 0·000040 molar solution. $x_0=0·000020$.

Time (hours).	Mols. I_2 per litre.	x.	$k=\frac{1}{ct} ln \frac{x}{0·000020}$.
0	0·003891	0	—
92	0·003598	0·000293	0·107
139	0·002870	0·001021	0·104
162½	0·001882	0·002009	0·104
169	0·001536	0·002355	0·1035

A second experiment, in which the quantity of sodium hydroxide added corresponded with 0·000080 mol. per litre, gave $x_0=0·000018$.

By reason of the rapid decomposition of the alkali hydroxide, these experiments cannot throw much light on the question of the nature of the isomeric change in the initial stages of the autocatalysis or of the occurrence and velocity of the reaction in neutral or slightly alkaline solution. Further experiments were therefore directed to the investigation of the progress of the change in solutions to which small quantities of the alkali salt of a weak acid were added. Sodium acetate was chosen for this purpose.

In presence of small quantities of sodium acetate, the reaction takes place very slowly, and there is no evidence of any auto-acceleration until the quantity of hydrogen iodide formed approaches that of the sodium acetate present. Up to this point the speed of the reaction is practically constant, straight lines being obtained when the iodine concentration is plotted against time. During the first period of observation the fall in the iodine concentration is somewhat greater than would be expected from the observed changes in the following periods, but this may be due to the action of iodine on traces of impurities in the solution.

The following data were obtained in two experiments, which were carried out simultaneously. Blank experiments without acetone showed that the action of iodine on the sodium acetate was not such as to interfere with the success of the measurements.

TABLE VII.

Solution as in experiment 1, with sodium acetate to give a 0·0008 molar solution.

Time (hours).......	0	72	115	163	240
Mols, I_2 per litre..	0·003981	0·003833	0·003775	0·003715	0·003597

Constant speed reaction.

Time (hours)	408	457	474
Mols. I_2 per litre..	0·002890	0·001369	0·000125

Autocatalytic change.

Solution as in experiment 1, with sodium acetate to give a 0·0012 molar solution.

Time (hours).......	0	72	115	163	240	408
Mols. I_2 per litre..	0·003971	0·003789	0·00373	0·003668	0·003565	0·003318

Constant speed reaction.

Time (hours)......	624	672	691
Mols. I_2 per litre.	0·003558	0·001479	0·000490

Autocatalytic change.

Neglecting the first time interval, and correcting the change in the iodine concentration during the uniform speed period for the loss of iodine found in the blank experiments, the constant rate of change as measured by $\Delta x/\Delta t$ is $1{\cdot}32 \times 10^{-6}$ mol. per litre per hour according to the first experiment, and $1{\cdot}24 \times 10^{-6}$ according to the second. A third experiment in which the conditions were exactly the same, except that the concentration of the sodium acetate was 0·0012 molar, gave $\Delta x/\Delta t = 1{\cdot}2 \times 10^{-6}$. As the mean value for a solution containing 20 c.c. of acetone per litre, we may therefore take $\Delta x/\Delta t = 1{\cdot}25 \times 10^{-6}$ mol. per litre per hour.

From experiments with the same acetone solution and hydrogen chloride as catalyst, it has been found that $\Delta x/\Delta t = 450 \times n \times 10^{-6}$ mol. per litre per minute, where n is the number of mols. of hydrogen chloride per litre. This corresponds with $0{\cdot}027n$ mol. per litre per hour, and from this it follows that the halogen acid concentration which corresponds with the observed reaction velocity in presence of small quantities of sodium acetate is equal to $1{\cdot}25 \times 10^{-6}/0{\cdot}027 = 0{\cdot}000046$ mol. per litre. The speed of the reaction in dilute sodium acetate solution is therefore more than twice as great as the initial speed with which the reaction appears to start in "neutral" solution, for this has been shown to correspond with a halogen acid concentration equal to 0·00002 mol. per litre.

As a consequence of hydrolysis, the sodium acetate solution represents a very slightly alkaline solution, and if the possible disturbing influence of the iodine is disregarded, the alkalinity may be calculated from the hydrolytic constant. For the mean sodium acetate solution (0·0012 mol. per litre), the hydroxyl ion concentration is thus found to be $1{\cdot}0 \times 10^{-6}$, which is about ten times the value of the ion concentration of pure water. Since the velocity of the reaction appears to be the same in all three experiments in spite of a variation of the sodium acetate concentration in the ratio 1 to 2, it does not seem probable that the observed rate of change can be ascribed entirely to the catalytic action of the hydroxyl ions. The fact that the constant speed interval extends over a period during which the sodium acetate concentration undergoes a very considerable diminution, points to the same conclusion.

It will now be convenient to recall the chief observations relating to the keto → enol transformation which have to be accounted for, namely, (1) that the reaction in "neutral" solution appears to start with a velocity considerably in excess of that corresponding with the acidity of the solution, (2) that the activity of the agent operative in "neutral" solution is apparently repressed by the addition of small quantities of mineral acid, and (3) that the reaction proceeds at a constant rate in the solution to which a small quantity of the alkali salt of a weak acid has been added.

Apart from the established activity of the acids as catalysts in the isodynamic transformation of the aliphatic ketones, certain facts seem to show that bases may play a similar part, although the nature of the experiments described in this paper, in which a halogen is employed as the indicator of the progress of the isomeric change, precludes the systematic investigation of this group of catalysts. If k_1 and k_2 denote the specific catalytic activities of the hydrogen and hydroxyl ions in a given acetone solution, then the rate of change due to the action of these will be given by $dx/dt = k_1 . c_H + k_2 . c_{OH}$. From the data for a solution containing 20 c.c. acetone per litre, $k_1 = 0{\cdot}027$ mol. per litre per hour. If it is assumed, for the moment, that the reaction in sodium acetate solution is chiefly due to the influence of the hydroxyl ion, then $k_2 = 1{\cdot}25$ mol. per litre per hour, and the ratio k_2/k_1 is therefore of the order of fifty. The observed facts cannot, however, be satisfactorily interpreted in terms of these two catalytic activities, and it seems quite certain that some other substance is active in promoting the isomeric change of the ketone in aqueous solution. The most likely constituent is the water forming the solvent medium. Although this view is put forward tentatively, it may be recalled that the assumption of a similar catalytic action has been found necessary by Lowry (Trans., 1903, **83**, 1314) in order to account for the phenomena observed in the mutarotation of aqueous solutions of dextrose. This change, which is accelerated by small quantities of acids and to a much greater extent by alkalis, cannot be prevented by neutralisation of the acid or basic impurities, and Lowry therefore supposes that the solvent, independently of its ionising properties, is directly concerned in the isomeric change.

It should be possible to evaluate the specific catalytic activity of the non-ionised water, and express it in terms of that of halogen acid, but this cannot be done satisfactorily with the data at disposal.

The Autocatalytic Change in Non-aqueous Solvents.—With the object of comparing the behaviour of water with that of other solvents, autocatalytic experiments have also been made in ethyl alcohol, toluene, and carbon tetrachloride solutions. The alcohol was freed from water by repeated treatment with metallic calcium, and the two other solvents were purified with great care.

When the action in these non-aqueous solvents is compared with that in water, very marked differences are apparent. In the first place, the reaction is incomplete, a considerable proportion of the iodine remaining unchanged even when very small quantities are added to the acetone solution. Secondly, the rate of change is not at all proportional to the concentration of the halogen acid, but increases much more rapidly than the latter. The connexion between the velocity and the halogen acid concentration is not deducible from the experimental results, and on this account the data cannot be extrapolated so as to obtain a value for the initial speed of the reaction in the pure non-aqueous solvent. A third difference is to be found in the relatively high speed of the reaction in non-aqueous solvents. The surprisingly large catalytic activity of the halogen acids in such non-ionising liquids as toluene and carbon tetrachloride is, no doubt, mainly responsible for the much shorter duration of the period required for the autocatalytic transformation of a given quantity of ketone, when dissolved in solvents of this class, as compared with the corresponding period of autocatalytic change in aqueous solution at the same temperature.

The following are the chief results obtained in this investigation:

(1) The progress of the auto-accelerated reaction between acetone and iodine in aqueous solution has been examined, and found to proceed in accordance with the assumption that three consecutive reactions are involved, the second and third being of relatively high speed in comparison with the primary isomeric change.

(2) An examination of the conditions under which the reaction occurs indicates that the presence of an acid catalyst is not essential. Although bases probably act as catalysts, it is not possible to explain the observations in aqueous solutions in terms of hydrogen and hydroxyl ion concentrations, and the suggestion is made that non-ionised water molecules also play an active part in the isodynamic change of the ketone.

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CLXIII.—*The Absorption Spectra of Some Substances Containing Two Benzene Nuclei.*

By John Edward Purvis and Nial Patrick McCleland.

In this communication the authors give an account of a comparative study of the absorption spectra of some of the simpler substances consisting of two benzene nuclei united by a chain of simple groups; for example, diphenylmethane, benzophenone, hydrazobenzene, and so on.

The investigation was carried out to discover, if possible, how far the vibrations of the two nuclei influence one another, and how they are affected by the nature of the groups uniting them; and, in particular, to study the effect of screening when there is present in the connecting chain a group which itself has power to produce vibrations. Having this object in view, the authors have examined the absorption spectra of the following substances in the usual way: diphenylmethane, phenyl-2:4-xylylmethane, benzophenone, phenyl benzyl ketone, dibenzyl ketone, diphenylamine, benzylaniline, dibenzylamine, diphenyl ether, phenyl benzyl ether, hydrazobenzene, and azobenzene. The absorption spectra of diphenyl and dibenzyl have also been examined by Baly and Tuck (Trans., 1908, **93**, 1913), and of $\alpha\delta$-diphenylbutane by Ebert and Stobbe (*Ber.*, 1911, **44**, 1292).

The following metallic derivatives were also examined: mercury diphenyl, mercury dibenzyl, arsenic triphenyl. All the above were carefully purified before they were examined, and the solutions were all freshly made up. If no solvent is mentioned the substance was dissolved in alcohol.

The authors are indebted to Mr. C. S. Gibson and Mr. T. F. Winmill for pure specimens of mercury dibenzyl and arsenic triphenyl respectively.

The cadmium spark was used as the source of radiant energy; but as it was sometimes thought that faint bands were obscured by the strong lines of the cadmium spectrum, in many cases the uranium-molybdenum spark was used in addition.

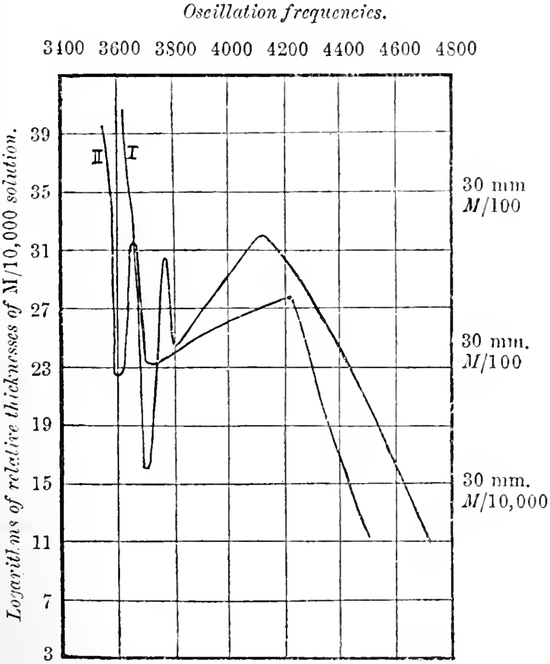
An attempt was made to study the absorption of the vapours, but owing to the lack of volatility only anisole was observed successfully.

Description of the Absorption Spectra.

Diphenyl.—This substance was examined by Baly and Tuck (*loc. cit.*). No bands were observed, but there was in $M/1000$-solution an extension of the line at about 3900 (oscillation frequencies).

Diphenylmethane (Fig. 1, I).—This substance shows two bands, a sharp band at 3700, and a somewhat wide one at 3800. These merge into one another as the concentration increases. The absorption spectrum of this substance has been examined by F. Baker (Trans., 1907, **91**, 495). He, however, only found one band in alcoholic solution similar to the wide band found by the authors. The substance used in the present investigation was most carefully purified by repeated crystallisation from alcohol, and was obtained in long, colourless crystals having the correct melting point.

Fig. 1.



I. *Diphenylmethane.*
II. *Phenyl-2 : 4-xylylmethane.*

Phenyl-2:4-xylylmethane (Fig. 1, II).—The curve is similar to the preceding, shifted, however, towards the less refrangible part. The persistency is much diminished, especially that of the band on the more refrangible side.

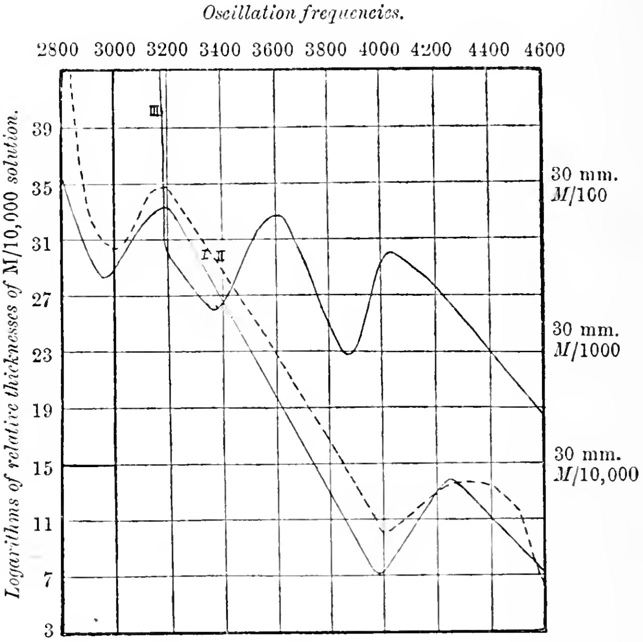
Dibenzyl.—This substance was examined by Baly and Tuck (*loc. cit.*). Two bands were found with heads at 3400 and 3800 (oscillation frequencies) respectively.

αδ-Diphenylbutane.—Ebert and Stobbe (*loc. cit.*) describe one band with its head at about 3800.

Benzophenone (Fig. 2, I).—The absorption curve exhibits in $M/100$-solution a band at 2960, and there is also a band at 3980 in the very dilute solution. It may be mentioned that Crymble, Stewart, and Wright have shown (Trans., 1911, **99**, 458) that solutions of benzophenoneoxime have no bands.

Phenyl Benzyl Ketone (Fig. 2, II).—There is a band at 3000 in the $M/100$-solution, and a very weak band at 4000 in $M/10,000$. The curve is very similar to that of benzophenone.

Fig. 2.



I. *Benzophenone.*
II. *Phenyl benzyl ketone* (broken line).
III. *Dibenzyl ketone.*

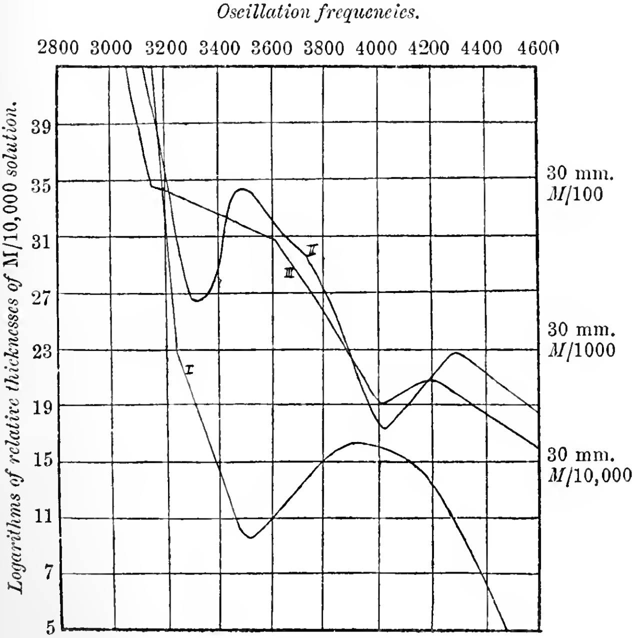
Dibenzyl Ketone.—This substance shows two large bands at 3350 and 3850 respectively.

Diphenylamine (Fig. 3, I).—The absorption spectrum of this substance has been examined by Baker (*loc. cit.*). The authors have repeated the observation, and have obtained results similar to those obtained by him.

The substance shows one strong wide band with its head at 3560. The band is not unlike that observed in the absorption spectrum of aniline by Baly and Collie (Trans., 1905, **87**, 1343), but it appears at somewhat greater dilution.

Benzylaniline (Fig. 3, II).—The curve shows two bands, one at 3300 corresponding with the band in the same place in diphenylamine, but appearing now in much stronger solution, and a band at 4020. The yellow colour of this substance appears to be due to general absorption in the visible regions of the spectrum. No band has been detected in that neighbourhood.

FIG. 3.



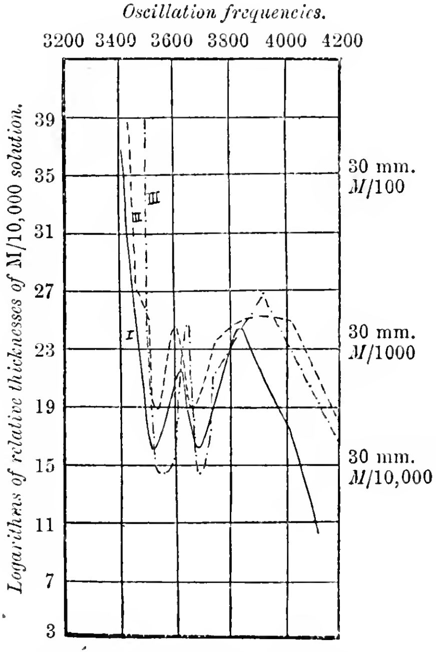
I. *Diphenylamine*
II. *Benzylaniline.*
III. *Dibenzylamine.*

Dibenzylamine (Fig. 3, III).—The absorption curve shows a rapid extension from 3200 to 3600, and a shallow band at about 4020.

Diphenyl Ether (Fig. 4, I).—It was found most convenient to examine this substance and the following in chloroform. The absorption curve of this substance shows two wide bands, the heads of which are at 3510 and 3690 respectively. These coalesce into one large band as the concentration increases. The curve of anisole in chloroform is also given (Fig. 4, III). This substance has been examined by Baly and Collie (Trans., 1905, **87**, 1342) in alcohol, and a similar result was obtained. It will be seen that the bands closely resemble those of diphenyl ether, but they are more persistent, and there is in addition a moderately rapid extension from 3740 to 3910.

Phenyl Benzyl Ether (Fig. 4, II).—Two bands were found in chloroform solutions of this substance, their heads being at 3540 and 3640. Their appearance is very similar to that of the bands of diphenyl ether and of anisole. There is also a slight extension of the curve between 3440 and 3510, and a rapid one between 3750 and 3900, corresponding with that of anisole in the same region, but much more marked.

FIG. 4.

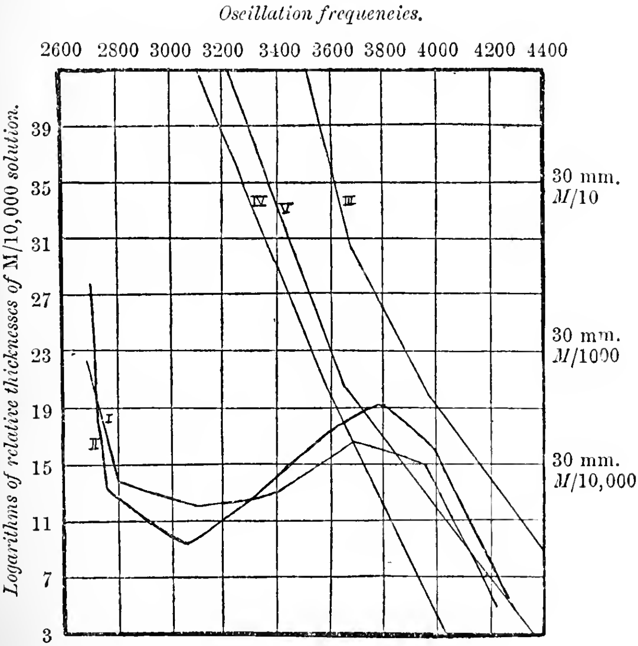


I. *Diphenyl ether* (full curve)
II. *Phenyl benzyl ether* (broken curve) } *in chloroform.*
III. *Anisole* (dot and dash curve)

Hydrazobenzene (Fig. 5, I).—This colourless substance oxidises somewhat rapidly even in chloroform solution, and becomes yellow. By working rapidly it was found possible to obtain evidence that only one shallow band exists.

Azobenzene (Fig. 5, II).—This substance has been examined in alcoholic solutions by Hartley (Trans., 1887, **51**, 152), and by Baly and Tuck (Trans., 1906, **89**, 982). The authors have repeated these observations in chloroform to compare the position and persistency of the band in the ultraviolet with that of the hydrazo-compound. As will be seen, the position of this band is practically the same in the two substances, but the persistency in the case of the azo-compound is far greater.

Fig. 5.



I. *Hydrazobenzene*
II. *Azobenzene*
III. *Mercury diphenyl*
IV. *Mercury dibenzyl*
V. *Arsenic triphenyl*
} *in chloroform.*

Chloroform solutions of mercury diphenyl, mercury dibenzyl, and arsenic triphenyl (Fig. 5, III, IV, and V) show no bands at any dilution. The great transparency of these substances, especially of mercury diphenyl, is remarkable.

Absorption bands of anisole vapour in a column 200 mm. long at various temperatures and pressures.

Abbreviations: v.w. = very weak; w. = weak; str. = strong; f. str. = fairly strong; narr. = narrow; diff. = diffuse.

	16°. 770 mm.		30°. 814 mm.		45°. 840 mm.	
	λ.		λ.		λ.	
A.	2786	v.w., narr.	2786	w.	2786	w., f.wide
	2780	,, ,,	2780	v.w.	2780	v.w.
	2776	,, ,,	2776	w., f.wide	2776	w., f.wide
	2770	,, ,,	2770	w.	2770	f.str.
			2767	v.w.	2767	,,
	2768	,, ,,	2768	v.w.		
	2765	f.str.	2765	f.str.	2765	str., f.wide
	2756	w.				
	2754	f.str.				
	2749	v.str.	2749	v.str., v.wide	2749	v.str., v.wide.
			2741	v.w., narr.	2741	v.w., narr.
					2739	,, ,,
			2736	,, ,,		
B.	2731	w., narr.	2731	w., narr.	2731	w., v.wide
	2729	,, ,,	2729	,, ,,	2728	w., f.wide
	2722	,, ,,	2722	,, ,,	2722	,, ,,
	2719	,, ,,	2719	,, ,,	2719	to 2679 strong absorption of rays
	2713	str.				
	2710	str., wide	2710	str., wide		
	2695	f.str., ,,	2701 to 2681	a very strong diffuse band	2670	to 2655 wide band.
	2681	str., v.wide				
	2680	w., narr.	2680	w., narr.		
	2664	,, ,,	2664	,, ,,		
	2660	str., ,,	2660	str.		
	2655	v.w., narr.	2655	v.w.		

16°.		30°.		45°.	
λ.		λ.		λ.	
2644	str., wide	2644	str., wide	2651 to 2628	wide band
2642	f.str., narr.	2642	f.str., narr.		
2638	v.w.				
2628	f.str., wide	2628	f.str., v.wide		
2625	v.w., narr.			2623 to 2605	strong absorption of rays
2614	f.str., wide.				
2612	,, ,,	2612	f.str., diff.		
2611	v.w., narr.				
2605	f.str., narr.	2605	f.str., wide		
2597	,, ,,	2597	,, narr.	2597 to 2590	f. strong band.
2593	str., wide	2593	str., wide		
2590	w., narr.	2590	w. narr.		
2580	f.str., wide	2580	f.str., wide	2577	f.str., diff.
		2566	v.w., narr.		
2561	,, ,,	2561	f.str., wide	2561	f.str., wide
2551	,, ,,	2551	,, ,,	2551	,, ,,
2541	w.str., ,,	2541	w., ,,	2541	w., ,,
2539	v.w., narr.	2539	v.w., narr.	2539	w., narr.
		2537	,,		
2530	w., f.wide	2530	w., f.wide	2530	w., diff.
2528	v.w., ,,				
2516	v.w., diff.	2516	v., w.diff.	2516	v.w., diff.

The rays were then transmitted to about λ 2240, where general absorption began.	The rays were then transmitted to about λ 2250, where general absorption began.	The rays were then transmitted to about λ 2260, where general absorption began.
41 bands.	37 bands.	24 bands.

	60°. 870 mm.		75°. 900 mm.	90°. 946 mm.
λ.		λ.		λ.
2786	w., f. wide	2786	f.str., wide	Strong absorption of rays from λ 2798 to λ 2491, Cd. 2574 showing through. The rays were then faintly transmitted to λ 2300, where general absorption began.
2780	,, ,,	2780	,, ,,	
2776	,, ,,	2780	str., wide	
2770 to 2749.	A very strong wide band. Then diffuse absorption to 2583.		Then rays were partially absorbed to λ 2499, but the following bands were just visible :	
	Two bands were then observed :	2749		1 band.
2580	v.w., narr.	2552		
2578	,, ,,	2544		
	From this point to 2536 diffuse absorption, through which the following bands were distinguished :		Rays were then transmitted to 2290, where general absorption began.	
2552			6 bands.	
2543				
	The following were then observed :			
2531	v.w.			
2516	,,			
	Rays were then transmitted to 2570, where general absorption began.			
	12 bands.			

At the higher temperatures and pressures the bands appeared to be wider and more diffuse, and some of them also widened into each other; for example, the series of bands λ 2770—λ 2749, clearly visible at 16° and 770 mm., produced a strong wide band at 60° and 870 mm.; the series of bands λ 2719—λ 2681 at 16° and 770 mm. produced a strong wide band λ 2719—λ 2679 at 45° and 840 mm.; and at 90° and 946 mm. one large band from λ 2798—λ 2491 took the place of the numerous bands observed at 16° and 770 mm. between λ 2786 and λ 2516.

It is important to notice that the two groups of bands *A* and *B* appear to correspond with the two single solution bands at 1/λ 3560 and 1/λ 3680; and that the single large band at 90° and 946 mm. corresponds with the large solution band at the greater thicknesses.

The general phenomena are comparable with the differences observed in the solution and vapour bands of benzene and various derivatives, and described by Hartley (*Phil. Trans.*, 1907, *A*, **208**, 475) and Purvis (Trans., 1910, **97**, 1546; 1911, **99**, 811, 1699).

Discussion of Results.

The introduction of a second benzenoid nucleus into a molecule already containing one or more vibration centres may be expected to produce changes of several kinds in the absorption spectrum. In the first place, the "weight" of the new group will tend to shift the whole band system towards the less refrangible regions. Next, if a phenyl group were already present it might be expected that the intensity of the benzenoid vibrations would be greater, and bands would appear which previously were too faint to be observed. This expectation, however, is not likely to be realised unless the newly introduced phenyl group were sufficiently screened from the other vibrating nuclei, because its unsaturation would be a disturbing factor to the vibrations existing in the original molecule. Lastly, the introduction of another vibration centre may be expected to have a great influence on the frequencies of the vibrations already existing in the molecule, apart from considerations of weight. It is well known that if there are two simultaneous vibrations in a system they will have this influence on one another, namely, that the vibrations which (independently) are more rapid will become faster, and those which are less rapid will become slower; and therefore in the case of vibrations in a molecule the probable result will be the thrusting apart of the bands due to the oscillation centres. This effect, coupled with that due to the weighting, will bring about the alteration that the bands due to the more rapid oscillations, which are usually some, at any rate, of those due to the benzene nucleus, will be altered only slightly in position; whilst the bands due to other nuclei (as, for example, the carbonyl group) will be displaced considerably towards the less refrangible regions; and this effect will be greatest when a benzene nucleus is most nearly situated to the other. This effect is very marked in the case of benzophenone.

Considering now the hydrocarbons, it is seen that in diphenyl, where the two nuclei are close together, the vibrations are almost entirely destroyed. There is just a slight extension of the curve to show that they are not altogether quiescent. In diphenylmethane, on the other hand, where there is sufficient freedom for vibration, the bands are well developed. The nuclei are, however, some distance apart, and the thrusting apart of the bands is not very noticeable. Now, as the connecting chain increases in length, the nuclei approach one another; so that in dibenzyl there are two large bands (each of which may be considered due to a benzene nucleus) with their heads about 400 units apart.

As the number of methylene groups increases, the slight unsaturation of this group, as evidenced by changes in the refractive power (Eykman, *Rec. trav. chim.*, 1893, **12**, 156), may deaden the vibrations; the lengthening of the chain also brings the nuclei into propinquity, with the result that the bands rapidly weaken and disappear. That the persistency of the bands in diphenylmethane is due to the combined effects of the two nuclei is made more probable by the spectrum of phenyl-2:4-xylylmethane. On introducing methyl groups into one of the nuclei, the oscillations of that nucleus are deadened, so that the bands, due to the combined effect of the two, lose in persistence.

In the three series of ketones, amines, and ethers, many points of interest are to be found. It will be seen that in the ketones and amines there is a band characteristic of the series and persisting throughout; although, in dibenzylamine it is very faint, and represented merely by a rapid extension. This band may be attributed to the carbonyl group in the one case and the nitrogen in the other.

For the position of the band due to the carbonyl group in the free state reference may be made to the study of aliphatic ketones by Stewart and Baly (Trans., 1906, **89**, 489). These authors find a band with the head at 3800 in solutions of acetone, and at about 3700 in those of methyl hexyl ketone. If allowance is made for greatly increased weighting, the band is quite analogous to that at 3350 in dibenzyl ketone. Stewart and Baly consider that the band is due to isorropesis between the carbonyl group and the adjacent methyl. The present authors suggest that it is equally valid to state that it may be caused by the vibrations within the carbonyl groups themselves.

In the case of the amines, also, the authors suggest that the large band is the result of the oscillatory effect caused by the unsaturated condition of the nitrogen atom; this view is supported by the fact that the same band is found throughout the series aniline, diphenylamine, triphenylamine, and in ethyl- and diethylaniline and benzylamine, etc. (Purvis, Trans., 1910, **97**, 1554).

In hydrazobenzene there are two NH-groups close together, and we may expect to find that they produce the same effect on one another as do the two phenyl nuclei in diphenyl; in fact, it is found that the band due to the unsaturation of the nitrogen has almost disappeared. In azobenzene, however, the nitrogen is so unsaturated that the band is quite strong. In this substance the complex ·N:N· also may function as an oscillation centre, and the colour may be ascribed to this cause.

Turning now to the ethers, it will be noticed that in diphenyl ether and in phenyl benzyl ether there are two bands similar to those in anisole. If anisole and diphenyl ether are compared, it will be apparent that the oscillations of the latter are greatly disturbed by the introduction of the second phenyl nucleus, as shown by the lessened persistency of the bands and by the disappearance of the extension. This effect is not unlike that noticed in diphenyl.

On the other hand, in phenyl benzyl ether, one of the phenyl nuclei is comparatively free as compared with the other; hence there appears a potential band or series of bands denoted by the rapid extension from 3750 to 3900.

In the metallic compounds the heavy atom in the case of arsenic (and perhaps also of mercury) is considerably unsaturated, and it entirely dislocates the movements of the phenyl nuclei, but is not able to replace them by others. Consequently, as is suggested by the great transparency of the solutions, there may be complete absence of vibration, at any rate in the ultraviolet regions.

The apparatus used was purchased through the assistance of the Government Grant Committee of the Royal Society, to whom the authors desire to express their thanks.

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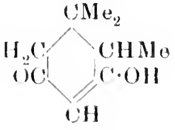
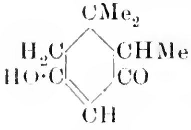
Cambridge.

CLXIV.—*Acyl Derivatives of the Dihydroresorcins. Part I. The Action of Hydroxylamine and of Phenylhydrazine on C-Acetyldimethyl- and C-Acetyltrimethyl-dihydroresorcins.*

By Arthur William Crossley and Nora Renouf (Salters' Fellow).

In a paper describing the preparation and properties of 1:1:2-trimethyl*cyclo*hexan-3-one from trimethyldihydroresorcin (Trans., 1911, **99**, 1101), it was pointed out that this dihydroresorcin is a tautomeric substance exhibiting the two forms represented by the formulæ (I) and (II), the particular form manifested depending


(I.)

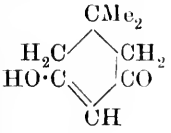

(II.)

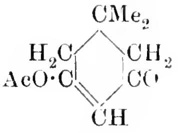
on the nature of the reagents with which it is brought in contact. With aniline, for example, it gives rise to only one anilide, which, like the corresponding derivative of dimethyldihydroresorcin, produces a colour with ferric chloride, thus showing its enolic nature.

It was thought that further information on this point might be obtained by an investigation of *C*-acetyltrimethyldihydroresorcin, which it was hoped to isolate in two forms. As in the case of the anilide, however, only one form has been encountered, so that, as far as the tautomerism of trimethyldihydroresorcin is concerned, no further evidence is provided. It was, however, decided to investigate this substance and also *C*-acetyldimethyldihydroresorcin fully, for they seem likely to prove of interest as throwing light on the behaviour of certain other compounds now under investigation.

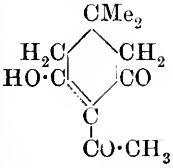
Dieckmann and Stein (*Ber.*, 1904, **37**, 3380) have described the *C*-acetyl derivative of dimethyldihydroresorcin, and have prepared from it a monoanilide and a substance melting at 190°, which they consider to be the phenylhydrazone of the phenylpyrazole derivative.

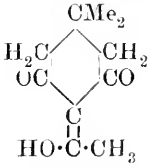
Dimethyldihydroresorcin (III) is easily converted into its


(III.)

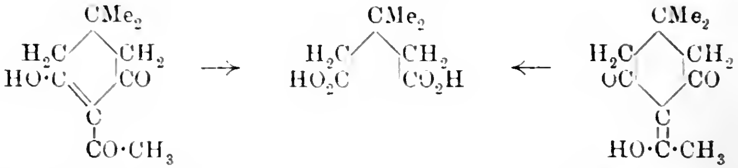

(IV.)

O-acetyl derivative (IV) by heating with acetic anhydride; but if a small quantity of sodium acetate is added, then the acetyl group wanders into the ring and *C*-acetyldimethyldihydroresorcin is produced. There are obviously two formulæ (V or VI) which may represent the structure of this substance, and from the present work the second one (VI) seems to be the more probable:

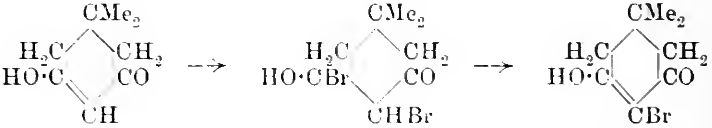

(V.)


(VI.)

Evidence for the existence of a hydroxyl group in *C*-acetyldimethyldihydroresorcin is afforded by the production of a colour with ferric chloride, the formation of an anilide, *p*-toluidide, methyl ether, etc., and by titration with sodium hydroxide, when it behaves as a monobasic acid, all properties in which it is similar to dimethyldihydroresorcin; but these facts do not help to decide between formulæ (V) and (VI), nor does the oxidation of the *C*-acetyl derivative with ordinary oxidising agents, when ββ-dimethylglutaric acid is produced, that is, the same product as is given by dimethyl-



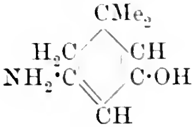
dihydroresorcin itself. It is hoped that experiments now being carried out, using ozone as oxidising agent, will give more definite information on this point. One striking difference between dimethyldihydroresorcin and its *C*-acetyl derivative is afforded by their behaviour towards bromine, the former readily adding on two atoms with subsequent elimination of hydrogen bromide and formation of bromodimethyldihydroresorcin (VII), whereas *C*-acetyldimethyldihydroresorcin does not absorb bromine in the slightest degree, not even when the solution in chloroform is boiled with a chloroform solution of bromine:



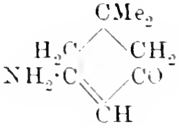
(VII.)

If *C*-acetyldimethyldihydroresorcin were represented by formula (V), there would not appear to be any reason why it should not behave towards bromine in an exactly similar manner to dimethyldihydroresorcin, whereas if formula VI is taken to represent its constitution, it would contain a double bond outside the ring, and as has been frequently noticed in connexion with hydroaromatic substances, more particularly terpene derivatives, in such cases bromine is only added on with great difficulty or not at all.

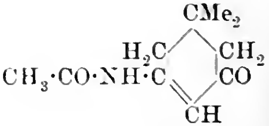
Further, Haas (Trans., 1906, **89**, 189) has shown that the monoamine, anilide, and *p*-toluidide of dimethyldihydroresorcin all give colour reactions with ferric chloride, which he ascribes to the fact that the monoamine is represented by formula VIII, and not by formula IX:



(VIII.)



(IX.)

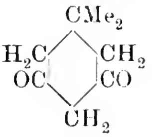


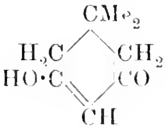
(X.)

These substances, however, no longer give colours with ferric chloride after acetylation, but do give semicarbazones, thus tending to show that the acetyl derivatives have formulæ similar to X.

Again, if formula V represents the constitution of *C*-acetyldimethyldihydroresorcin, it would be expected to show a similar behaviour to dimethyldihydroresorcin in derivatives such as the monoamine, the anilide, and the *p*-toluidide; yet none of these substances gives colours with ferric chloride, nor do they yield acetyl derivatives, which is taken as a further proof in favour of formula VI.

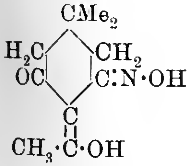
The dihydroresorcins behave towards hydroxylamine and phenylhydrazine as diketones (XI), despite the fact that towards the majority of reagents they react in the keto-enol form (XII):


(XI.)


(XII.)

It was therefore decided to investigate the action of hydroxylamine and phenylhydrazine on the *C*-acetyl derivatives of dimethyl- and trimethyl-dihydroresorcins in order to obtain further information as to their constitution.

When *C*-acetyldimethyldihydroresorcin is treated with hydroxylamine (the actual conditions are stated in the experimental portion of this paper), there are formed an acid oxime and an *iso*oxazole derivative (also an oxime of the *iso*oxazole with excess of hydroxylamine), the former very readily losing water to give the latter. There are several formulæ which may be ascribed to the acid oxime according as to whether formula V or VI is taken as representing *C*-acetyldimethyldihydroresorcin. Only two need be mentioned here, namely, XIII and XIV, either of which would give an *iso*oxazole derivative by loss of water. It is not possible at the present time to decide which formula* represents the *iso*oxazole formula; the former appears to be the more probable, but it is convenient to refer to the compounds as *iso*oxazoles. The corresponding pyrazoles are also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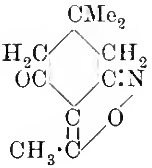
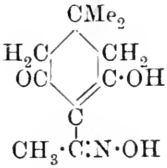
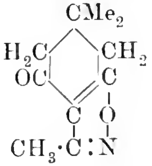



(XIV.)



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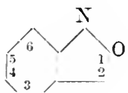
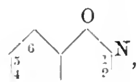
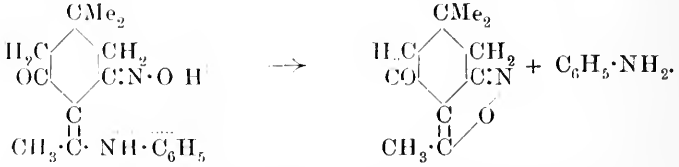
* That is, the ψ-oxazole, , or the *iso*oxazole, ,

derivative, and therefore no definite conclusion can be drawn as to the constitution of *C*-acetyldimethyldihydroresorcin.

The action of hydroxylamine on derivatives of *C*-acetyldimethyldihydroresorcin, such as the anilide, *p*-toluidide, and monoamine, was next tried, and again the same *iso*oxazole derivative is formed by elimination of either aniline, *p*-toluidine, or ammonia:



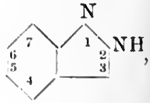
As only the *iso*oxazole derivative is produced under these conditions and no acid monoxime, it proves that the elimination of aniline is not due to simple hydrolysis of the anilide.

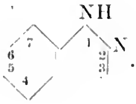
C-Acetyldimethyldihydroresorcin gives with phenylhydrazine an acid phenylhydrazone, a phenylpyrazole derivative, and a phenylhydrazone of the phenylpyrazole derivative. It may, however, be noted that formation of the pyrazole derivative does not appear to take place so readily in the cold as formation of the corresponding *iso*oxazole derivative, because there is a much larger proportion of the acid phenylhydrazone produced than of the acid oxime.

The phenylhydrazone of the phenylpyrazole (m. p. 190°) was described by Dieckmann and Stein (*loc. cit.*) as being prepared by heating together phenylhydrazine and *C*-acetyldimethyldihydroresorcin for a short time in alcoholic solution. It is now found that under these conditions only the phenylpyrazole, melting at 135°, is obtained, and in order to prepare the phenylhydrazone of this substance (m. p. 210°, not 190°), it is necessary to heat the components together in alcoholic solution to which a certain amount of acetic acid has been added.

Derivatives of *C*-acetyldimethyldihydroresorcin behave with phenylhydrazine apparently in a similar manner as they do towards hydroxylamine, the anilide giving rise only to the phenylpyrazole.

C-Acetyltrimethyldihydroresorcin, as already mentioned, exists only in one form, but which of the three following formulæ repre-

conveniently thus named, but here also the indazole formula, 

, appears more probable than the pyrazole, 

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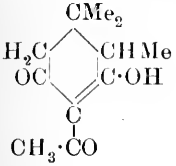
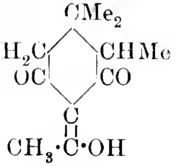
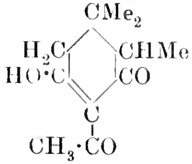
sents its structure it is impossible to say at the present time, although from the evidence forthcoming formula XV would appear





(XV.)



to be the most likely, on account of the similarity of it and its derivatives in chemical behaviour to *C*-acetyldimethyldihydroresorcin and its derivatives.

The action of hydroxylamine on *C*-acetyltrimethyldihydroresorcin was not studied in detail, as it was found that the *iso*oxazole was a liquid or a solid of very low melting point. With phenylhydrazine it gives an acid phenylhydrazone and a phenylpyrazole, but no evidence of the formation of a phenylhydrazone of the phenylpyrazole could be obtained.

The acid phenylhydrazone is very difficult to isolate unless the preparation is carried out under the conditions described in the experimental portion of this paper, as it is extremely easily converted into the phenylpyrazole by the merest trace of acid.

The anilide and monoamine of *C*-acetyltrimethyldihydroresorcin also give the phenylpyrazole when treated with phenylhydrazine, aniline or ammonia being eliminated.

EXPERIMENTAL.

C-Acetyldimethyldihydroresorcin was prepared according to the directions given by Dieckmann and Stein (*Ber.*, 1904, **37**, 3379). After removal of the excess of acetic anhydride from the crude acetylated product by distillation, the residue was dissolved in ether, the solution washed with sodium hydroxide (ethereal solution = *A*), and these washings worked up for the *C*-acetyl derivative. The final product was not purified by crystallisation from dilute acetic acid, as it was found that, on distillation in a vacuum, it passed over quite constantly at 138°/23 mm., solidified immediately on cooling, and was analytically pure. It behaves on titration as a monobasic acid, a reaction which is best carried out in alcoholic solution:

0·5664 required 31·5 c.c. $N/10$-NaOH. M.W. = 179·8.

$C_{10}H_{14}O_3$ requires M.W. = 182.

The yield of copper salt is somewhat larger than stated by Dieckmann and Stein, namely, 24—26 grams from 20 grams of dimethyldihydroresorcin, giving 15—16 grams (61 per cent. of the theoretical, calculated on the dimethyldihydroresorcin used) of the pure *C*-acetyl derivative. Like dimethyldihydroresorcin, it gives a colour reaction with ferric chloride, as described by Dieckmann and Stein (*ibid.*, p. 3381), but it differs from dimethyldihydroresorcin in not decolorising a chloroform solution of bromine even on boiling (compare Trans., 1899, **75**, 775).

The ethereal solution *A* (see above) was washed with water, dried, and evaporated to a small bulk, when a crystalline substance separated (3·1 grams from 80 grams of dimethyldihydroresorcin), which was purified by crystallisation from alcohol, and analysed:

0·1075 gave 0·2733 CO_2 and 0·0749 H_2O. C=69·33; H=7·74.

$C_{20}H_{26}O_5$ requires C=69·36; H=7·51 per cent.

The *anhydride* of *C*-acetyldimethyldihydroresorcin is readily soluble in the cold in benzene or chloroform, readily on warming in acetone, ethyl acetate, or alcohol, crystallising from either of the latter solvents in colourless, transparent, six-sided plates, melting at 194°. The alcoholic solution is neutral to litmus, and does not give a colour with ferric chloride. When heated with alcoholic potassium hydroxide solution, it is quantitatively converted into *C*-acetyldimethyldihydroresorcin.

Derivatives of C-*Acetyldimethyldihydroresorcin.*

The *silver* salt was prepared in the usual manner after careful neutralisation with aqueous sodium hydroxide solution, when it separated as a flaky, granular, white precipitate:

0·2003 gave 0·0750 Ag. Ag=37·44.

$C_{10}H_{13}O_3Ag$ requires Ag=37·37 per cent.

The *methyl ether*, obtained by heating the dry silver salt with methyl iodide in dry ethereal solution, is very readily soluble in the cold in chloroform and benzene, less soluble in alcohol and ethyl acetate, and crystallises from a mixture of chloroform and light petroleum (b. p. 40—60°) in stout, transparent, six-sided plates, melting at 93°:

0·1409 gave 0·3464 CO_2 and 0·1062 H_2O. C=67·05; H=8·37.

$C_{11}H_{16}O_3$ requires C=67·34; H=8·16 per cent.

The ether is very susceptible to the action of moisture, and although formed by direct esterification, it cannot be isolated from the product on this account. Moreover, it cannot be crystallised without first carefully drying the solvent.

The anilide (compare Dieckmann and Stein, p. 3381) is best prepared by heating with aniline in alcoholic solution. It crystallises in stout, colourless (not faintly yellow) needles, melting at 131°. Unlike the anilide of dimethyldihydroresorcin (compare

Haas, Trans., 1906, **89**, 202), it does not give a colour with ferric chloride, and does not form a hydrochloride, an acetyl derivative, or a dianilide. It dissolves appreciably in cold 10 per cent. potassium hydroxide solution, and completely on warming, about one-half being reprecipitated on acidification, the remainder having been hydrolysed, whereas the anilide of dimethyldihydroresorcin is completely insoluble in potassium hydroxide solution. It gives a neutral alcoholic solution, but on keeping or on adding a few drops of water an acid reaction is developed, probably due to hydrolysis, as the anilide is extremely easily hydrolysed by 5 per cent. sulphuric acid in alcohol, giving a quantitative amount of *C*-acetyldimethyldihydroresorcin. Haas (Trans., 1906, **89**, 205) has shown that dimethyldihydroresorcin does not react with methylaniline, nor does the *C*-acetyl derivative under the same conditions, or when the two substances are heated in dry benzene solution or in alcoholic solution in presence of either zinc chloride or sodium ethoxide.

The p-*toluidide* prepared in a similar manner to the anilide, is soluble in the cold in chloroform, readily on warming in benzene, acetone, or ethyl acetate, and crystallises from ethyl alcohol in stout, colourless, transparent, flattened needles, melting at 138°:

0·2025 gave 8·8 c.c. N_2 (moist) at 14° and 756 mm. N = 5·08.

$C_{17}H_{21}O_2N$ requires N = 5·16 per cent.

The properties of the *p*-toluidide are in every way similar to those of the anilide.

The *monoamine* prepared by dissolving the *C*-acetyl derivative in concentrated ammonium hydroxide solution and evaporating to dryness on the water-bath, is readily soluble in the cold in chloroform, alcohol, acetone, or ethyl acetate, readily on warming in water or benzene, from either of which solvents it crystallises in radiating clusters of fine, colourless needles, melting at 133°:

0·1562 gave 10·2 c.c. N_2 (moist) at 22° and 770 mm. N = 7·50.

$C_{10}H_{15}O_2N$ requires N = 7·73 per cent.

It does not give an acetyl derivative, is insoluble in cold dilute sodium hydroxide solution, readily, however, on warming, with hydrolysis. It is soluble in water to give a neutral solution, which does not give a colour with ferric chloride, and although readily soluble in cold dilute hydrochloric acid, no evidence of the formation of a stable hydrochloride could be obtained; thus it shows a marked difference in properties from the monoamine of dimethyldihydroresorcin (compare Haas, *ibid.*, p. 192).

Action of Hydroxylamine on C-*Acetyldimethyldihydroresorcin.*

Nine grams of the *C*-acetyl derivative (1 molecule) were dissolved in alcohol, 3·5 grams of hydroxylamine hydrochloride (1 molecule) dissolved in a small amount of water added, the whole neutralised with sodium hydroxide, and allowed to remain for three days. The solution was then poured into water, extracted six times with ether, etc. (aqueous liquid = *B*), when on evaporating the ether 4 grams of a white solid were obtained, which was purified by crystallisation from light petroleum, and analysed:

0·2202 gave 14·8 c.c. N_2 (moist) at 13° and 746 mm. N = 7·79.
$C_{10}H_{13}O_2N$ requires N = 7·82 per cent.

3-*Keto*-2 : 5 : 5-*trimethylhexahydrobenz*iso*oxazole* * is readily soluble in the cold in the ordinary organic solvents except light petroleum (b. p. 40—60°), from which it crystallises in radiating clusters of colourless, flattened needles, melting at 55—56°. A solution of the substance in alcohol is neutral to litmus, and gives no colour with ferric chloride. It does not decolorise a solution of bromine in chloroform, does not give a benzoyl derivative, and dissolves in cold concentrated sulphuric acid, without, however, producing any colour. It is slowly attacked by potassium permanganate in the cold, and the principal oxidation product is *as*-dimethylsuccinic acid.

The *oxime* of ketotrimethylhexahydrobenz*iso*oxazole was prepared by heating together 1 molecule of *C*-acetyldimethyldihydroresorcin, 3 molecules of hydroxylamine hydrochloride, and 3 molecules of glacial acetic acid in absolute alcoholic solution, or by heating 1 molecule of ketotrimethylhexahydrobenz*iso*oxazole with 2 molecules of hydroxylamine hydrochloride and 2 molecules of glacial acetic acid in alcoholic solution for two hours. The alcohol was evaporated and water added, when a solid separated, which was purified by crystallisation from alcohol:

0·1151 gave 14·6 c.c. N_2 (moist) at 20° and 750 mm. N = 14·32.
$C_{10}H_{14}O_2N_2$ requires N = 14·43 per cent.

The oxime is very readily soluble on warming in ethyl acetate, chloroform, or acetone, less readily so in benzene or alcohol, crystallising from either of the latter solvents in rosettes of silken needles melting at 192°, with decomposition and evolution of gas, although the actual temperature varies somewhat with the rate at which the heating is carried out. The oxime dissolves in cold concentrated sulphuric acid without, however, giving any colour.

The aqueous liquid *B* (see above) was acidified with dilute

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* See footnote on p. 1527.

sulphuric acid, when 3 grams of a solid were precipitated (acid liquid = *C*), which, after well washing with water, was crystallised from benzene and analysed:

0·1578 gave 9·2 c.c. N_2 (moist) at 9° and 766 mm. N = 7·06.
$C_{10}H_{15}O_3N$ requires N = 7·10 per cent.

The *monoxime* of *C*-acetyldimethyldihydroresorcin is insoluble in light petroleum, readily soluble on warming in alcohol, ethyl acetate, acetone, or chloroform, and crystallises from benzene in radiating clusters of nacreous needles, melting at 115°, with vigorous evolution of gas. The melting point varies a few degrees either way, according to the rate of heating, because the melting point is also a decomposition point, where water is evolved with formation of ketotrimethylhexahydrobenz*iso*oxazole, melting at 55—56°. The monoxime shows marked acid properties, and can be titrated with sodium hydroxide, using phenolphthalein as indicator. The reaction is best carried out in alcoholic solution, and the oxime must be dissolved in the cold, otherwise a certain proportion is transformed, by loss of water, into the benz*iso*oxazole derivative:

0·3392 required 17·4 c.c. *N*/10-NaOH. M.W. = 195.
$C_{10}H_{15}O_3N$ requires M.W. = 197.

An attempt to prepare an anilide of this acid oxime was unsuccessful, the result being loss of water and formation of the corresponding ketotrimethylhexahydrobenz*iso*oxazole.

The acid liquid *C* (see above) was again extracted with ether, when a further 3·6 grams of ketotrimethylhexahydrobenz*iso*oxazole were obtained, which must have been produced from the acid monoxime on acidifying with sulphuric acid. The conversion of the acid monoxime into the *iso*oxazole derivative is very readily brought about by acid, and hence the reason for stating above that the crude oxime must be well washed with water to remove acid, previous to crystallisation; otherwise, during the process a very large proportion is converted into the *iso*oxazole. The above 1·6 grams of ketotrimethylhexahydrobenz*iso*oxazole, together with the 4 grams originally extracted, and the 3 grams of the acid monoxime, account for the whole of the *C*-acetyldimethyldihydroresorcin used in the experiment.

Action of Hydroxylamine on Derivatives of C-*Acetyldimethyldihydroresorcin.*

Seven and a-half grams of the anilide of *C*-acetyldimethyldihydroresorcin (1 molecule) were dissolved in alcohol, and to the cold solution 4·2 grams of hydroxylamine hydrochloride (2 molecules), dissolved in water, added, the solution neutralised with sodium hydroxide, and allowed to remain for three days. The whole was then poured into water, extracted with ether, the ethereal solution washed with dilute sulphuric acid (washings = *D*), sodium hydroxide, then water, dried, and evaporated, when 4·8 grams (theory, 5·2) of ketotrimethylhexahydrobenz*iso*oxazole were obtained.

The acid washings *D* yielded 2·6 (theory, 2·7) grams of aniline, identified by converting it into acetanilide.

The same result is obtained when the anilide is dissolved in absolute alcohol, 1 molecule of dry powdered hydroxylamine hydrochloride and 1½ molecules of dry powdered potassium acetate added, and the whole allowed to remain for three days.

The *p*-toluidide and monoamine were treated with hydroxylamine under similar conditions to those described in the case of the anilide, and with a similar result, namely, the production of a quantitative amount of ketotrimethylhexahydrobenz*iso*oxazole and liberation of either *p*-toluidine or ammonia.

Action of Phenylhydrazine on C-Acetyldimethyldihydroresorcin.

Nine grams of *C*-acetyldimethyldihydroresorcin (1 molecule) were dissolved in alcohol, 5·4 grams (1 molecule) of phenylhydrazine added, and the whole allowed to remain for three days. The solution was poured into water, extracted with ether, the ethereal solution washed with dilute sulphuric acid, sodium hydroxide (washings = *E*), and water, then dried, etc., when 3·1 grams of a solid were obtained, which after purification was analysed:

0·1647 gave 15·8 c.c. N_2 (moist) at 19° and 760 mm. N = 11·03.

$C_{16}H_{18}ON_2$ requires N = 11·02 per cent.

This same substance can be obtained in almost quantitative amount by heating 1 molecule of *C*-acetyldimethyldihydroresorcin with 1 molecule of phenylhydrazine in absolute alcoholic solution for two hours.

4-*Keto-2-phenyl*-3 : 6 : 6-*trimethylhexahydrobenzopyrazole* * is insoluble in light petroleum, readily in the cold in chloroform, and on warming in benzene, ethyl acetate, or acetone, and crystallises from alcohol in stout, colourless, transparent rhombs, melting at 135°. The solution in alcohol has no acid reaction, it does not give a colour with ferric chloride, nor does the solid give a colour when dissolved in concentrated sulphuric acid.

The *phenylhydrazone* of ketophenyltrimethylhexahydrobenzopyrazole was prepared by heating 1 molecule of the pyrazole with 2 molecules of phenylhydrazine and 2 molecules of glacial acetic

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* See footnote on p. 1527.

acid in absolute alcoholic solution for two hours, during which time a large amount of solid separated, which was directly analysed after well washing with alcohol, as it cannot be purified by crystallisation owing to partial decomposition:

0·1632 gave 22·2 c.c. N_2 (moist) at 13° and 770 mm. N = 16·29.
$C_{22}H_{24}N_4$ requires N = 16·27 per cent.

The phenylhydrazone, the yield of which is quantitative, separates as above described in small, very faintly yellow, rhombic crystals, melting at 209—210°. It can also be produced in quantitative amount directly from *C*-acetyldimethyldihydroresorcin by heating with 3 molecules of phenylhydrazine and 3 molecules of glacial acetic acid in alcoholic solution. The phenylhydrazone dissolves in concentrated sulphuric acid, with production of a deep green colour, is almost insoluble in alcohol, not readily soluble in benzene, ethyl acetate, or acetone, fairly readily so in chloroform, but all solutions gradually become deep brown, and the chloroform solution finally becomes deep green.

The sodium hydroxide washings *E* (see p. 1534) were acidified, when 9·3 grams of solid separated, which, after being well washed with water, was purified by crystallisation from cold chloroform on addition of light petroleum (b. p. 40—60°):

0·1784 gave 15·2 c.c. N_2 (moist) at 15° and 770 mm. N = 10·11.
$C_{16}H_{20}O_2N_2$ requires N = 10·29 per cent.

The *phenylhydrazone* of *C*-acetyldimethyldihydroresorcin is readily soluble in the ordinary organic solvents, with exception of light petroleum, and crystallises from a mixture of chloroform and light petroleum (b. p. 40—60°) in radiating clusters of nacreous needles, melting at 98° with evolution of gas and production of ketophenyltrimethylhexahydrobenzopyrazole.

Like the acid monoxime (see p. 1533) this phenylhydrazone shows marked acid properties, and can be titrated in a similar manner, when it behaves as a monobasic acid:

0·2649 required 9·9 c.c. *N*/10-NaOH. M.W. = 267·4.
$C_{16}H_{20}O_2N_2$ requires M.W. = 272.

The action of phenylhydrazine on the anilide of C-*acetyldimethyldihydroresorcin* was investigated in the cold, and the product worked up as described (see p. 1534), when a practically quantitative yield of ketophenyltrimethylhexahydrobenzopyrazole melting at 135° was obtained, together with the corresponding quantity of aniline.

Preparation of C-Acetyltrimethyldihydroresorcin.

The preparation of this substance was carried out under exactly similar conditions to those described in the case of the corresponding derivative of dimethyldihydroresorcin (see p. 1529), except that in the preparation of the copper salt (yield, 18—20 grams from 20 grams of the dihydroresorcin) the whole was allowed to remain for twenty-four hours. The salt was purified by crystallisation from dilute alcohol, when it separated in small, stout, Prussian-blue needles, melting and decomposing at 210°:

0·2752 gave 0·0479 CuO. Cu = 13·88.

$(C_{11}H_{15}O_3)_2Cu$ requires Cu = 14·00 per cent.

C-Acetyltrimethyldihydroresorcin was prepared from the copper salt as described (see p. 1529), and purified by distillation under diminished pressure:

0·1351 gave 0·3336 CO_2 and 0·1009 H_2O. C = 67·34; H = 8·29.

$C_{11}H_{16}O_3$ requires C = 67·35; H = 8·16 per cent.

It is a clear, oily, refractive liquid, boiling at 153°/33 mm., and possessing a sharp odour reminiscent of fatty acids. It does not solidify on cooling to −17°; it behaves towards ferric chloride and bromine in an exactly similar manner to *C*-acetyldimethyldihydroresorcin, and titration shows its monobasic acid nature:

0·7683 required 40 c.c. *N*/10-NaOH. M.W. = 191·6.

$C_{11}H_{16}O_3$ requires M.W. = 196.

The *anilide*, which is obtained in practically quantitative yield, is readily soluble in the cold in chloroform, acetone, and ethyl acetate, readily on warming in benzene or alcohol, and crystallises from light petroleum (b. p. 80—100°) in compact masses of transparent, colourless crystals, melting at 91—92°:

0·2560 gave 11·4 c.c. N_2 (moist) at 21° and 770 mm. N = 5·13.

$C_{17}H_{21}O_2N$ requires N = 5·16 per cent.

In chemical behaviour it resembles exactly the anilide of *C*-acetyldimethyldihydroresorcin.

The *monoamine* is obtained in quantitative amount, and is readily soluble in the cold in acetone, ethyl acetate, chloroform, or alcohol, sparingly so in boiling water, and crystallises from benzene in colourless, nacreous plates, melting at 137°:

0·2415 gave 14·6 c.c. N_2 (moist) at 18° and 768 mm. N = 7·06.

$C_{11}H_{17}O_2N$ requires N = 7·17 per cent.

It is sparingly soluble in sodium hydroxide solution, but otherwise resembles the monoamine of *C*-acetyldimethyldihydroresorcin.

Action of Phenylhydrazine on C-*Acetyltrimethyldihydroresorcin.*

Four grams (1 molecule) of *C*-acetyltrimethyldihydroresorcin were heated with 2·1 grams (1 molecule) of phenylhydrazine in alcoholic solution for two hours, when most of the alcohol was evaporated, and a solid precipitated by the gradual addition of water. In all, 4·4 grams (81 per cent. of the theoretical amount) were obtained:

0·1480 gave 13·4 c.c. N_2 (moist) at 20° and 758 mm. N = 10·33

$C_{17}H_{20}ON_2$ requires N = 10·44 per cent.

4-*Keto*-2-*phenyl*-3 : 6 : 6 : 7-*tetramethylhexahydrobenzopyrazole* is readily soluble in the cold in chloroform, readily on warming in alcohol, ethyl acetate, acetone, or benzene, and crystallises from light petroleum (b. p. 80—100°) in colourless, transparent rhombs, melting at 125·5°. In chemical behaviour it resembles ketophenyltrimethylhexahydrobenzopyrazole, except that no indication of the formation of a phenylhydrazone could be obtained by the further action of phenylhydrazine. The reaction was carried out under a variety of conditions, but unchanged material was always recovered, and, in addition, when using excess of acetic acid and heating for some hours, the monoacetyl derivative of phenylhydrazine melting at 128·5° (compare Fischer, *Annalen*, 1878, **190**, 129).

In a second experiment the above-mentioned quantities of *C*-acetyltrimethyldihydroresorcin and phenylhydrazine in alcoholic solution were allowed to remain for three days. More alcohol was then added, and the whole carefully neutralised with sodium hydroxide solution, extracted with ether (alkaline liquid = *D*), washed with water, dried, and evaporated, when 1·4 grams of solid were obtained, which consisted of a mixture of ketophenyltetramethylhexahydrobenzopyrazole and the phenylhydrazone of *C*-acetyltrimethyldihydroresorcin (see below), as proved by the fact that on heating the mixture was completely converted into the pyrazole derivative.

To the alkaline liquid *D* a quantity of sulphuric acid was then added in not quite sufficient quantity to neutralise the sodium hydroxide previously added, when an oil separated, which immediately solidified (2·2 grams). The solid was purified by crystallisation from cold benzene and light petroleum (b. p. 40—60°), and analysed:

0·1065 gave 9·1 c.c. N_2 (moist) at 20° and 758 mm. N = 9·75.

$C_{17}H_{22}O_2N_2$ requires N = 9·79 per cent.

The *phenylhydrazone* of *C*-acetyltrimethyldihydroresorcin crystallises in clusters of transparent, flattened needles, melting at 118° with evolution of gas and formation of ketophenyltetramethylhexahydrobenzopyrazole. It behaves in a curious manner on titration with sodium hydroxide, using phenolphthalein or litmus as indicator, for if the addition of sodium hydroxide is stopped at the first appearance of an alkaline reaction, much too high a number is obtained for the molecular weight, which is explained by the fact that on extracting the liquid with ether, unchanged phenylhydrazone is obtained.

The action of phenylhydrazine on derivatives of C-*acetyltrimethyldihydroresorcin* (the monoamine and anilide) was examined, with the result that in each case ketophenyltetramethylhexahydrobenzopyrazole was formed, with liberation of either ammonia or aniline.

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CLXV.—*The Colouring Matters of the Flowers of the* Cedrela toona.

By Arthur George Perkin.

The *Cedrela toona*, the Toon or Indian mahogany tree, is a large tree usually from 50 to 60 feet, although occasionally reaching 100 feet, in height, the wood of which closely resembles mahogany, and is imported into England under the name of "Moulmein Cedar," and much used for making furniture. It occurs in the tropical Himalaya from the Indus eastward, throughout the hilly districts of Central and Southern India to Burma, and is also found in Java and Australia. The flowers, which constitute one of the less important natural Indian dyestuffs, are reputed to yield both a red and a yellow dye (known in Bengal as *Gunari*), which is applied without mordants. Although considerably employed alone, for dyeing purposes, the flowers are also used in Burma in conjunction with safflower and together with turmeric to produce the sulphur-yellow colour or "basanti" of Cawnpore. In the North-West Provinces the flowers are boiled with water to extract the dye, but the colour obtained on fabrics is not permanent, and appears to be only in request by the poorer classes. According to the late Sir Thomas Wardle, "these flowers contain a large quantity of yellow colouring matter"; "they appear well adapted for tasar silk." The seeds of the plant are also stated to yield a red dye (Watts' "Dictionary of the Economic Products of India," Vol. II.).

For a liberal supply of these flowers I am indebted to the kindness of Mr. T. H. Burkill, Reporter on Economic Products to the Government of India, and also to Mr. D. Hooper, the Officiating Reporter.

EXPERIMENTAL.

The flowers were extracted in quantities of 1 kilo. with 5 parts of boiling water for six hours, the mixture filtered, and the residue well pressed. The pale yellowish-brown extract was treated with 6 per cent. of hydrochloric acid (33 per cent.), and heated to 70—80° for six hours, causing the gradual separation of a finely-divided, reddish-brown precipitate. After remaining overnight, the clear liquid (*A*) was decanted off, the deposit collected, well washed, drained on a porous tile, and allowed to dry at the ordinary temperature. The powdered product (average 35 grams) was completely exhausted with boiling absolute alcohol, a considerable quantity (23 grams) of a brown residue (*B*) thus remaining undissolved. The alcoholic solution on gradual concentration to a small bulk deposited a minute amount of a red, microcrystalline powder, and this was collected by the aid of the pump by means of a funnel previously well warmed, and washed with hot alcohol. Yield, 0·18 gram. The filtrate, which on cooling gelatinised owing to the separation of plant wax, was now poured into some quantity of ether, the precipitated dark-coloured impurity removed, the liquid well washed with water, and evaporated to dryness. By addition of a little hot alcohol a further quantity (0·08 gram) of the red powder separated, which was collected in a similar manner. To eliminate wax, the filtrate was again poured into ether, the mixture shaken with dilute potassium hydroxide solution, the alkaline liquid at once neutralised with acid, and the dull orange-red precipitate collected. By redissolving in ether and evaporation, this product yielded a trace (0·038 gram) of the red compound, the filtrate (*C*) being reserved for further examination.

The crude red colouring matter, on solution in a little hot pyridine and removal of an insoluble amorphous impurity, separated out on cooling in the crystalline condition, and by a second similar treatment was obtained pure. Finally, it was washed several times with boiling benzene, and dried at 160°.

Found: $C = 72{\cdot}72$, $72{\cdot}66$; $H = 7{\cdot}81$, $7{\cdot}70$.

$C_{15}H_{18}O_3$ requires $C = 73{\cdot}17$; $H = 7{\cdot}31$ per cent.

This compound separates from pyridine in large, orange-coloured plates or leaflets, which contain pyridine, and become red and opaque when washed with benzene or alcohol, the pyridine being thus eliminated. Hot dilute alkalis dissolve it with an orange-yellow coloration, but with stronger solutions of the alkalis, alkali carbonates, and ammonia, the corresponding salts separate in the form of amorphous, yellow powders. It is very sparingly soluble in alcohol and the usual solvents, more readily in pyridine, and melts at 285—287°. With cold concentrated sulphuric acid, it produces a beautiful indigo-blue liquid, which on keeping becomes gradually brownish-yellow, and this characteristic reaction suggested at first that it might in reality be bixin, the red colouring matter from annatto, *Bixa orellana*.

The formula $C_{28}H_{34}O_5$, however, assigned to this compound by Etti (*Ber.*, 1874, **7**, 446; 1878, **11**, 864), and more recently adopted by Marchlewski and Matejko (*Bull. Acad. Sci. Cracow*, 1905, 745), is not in harmony with the analytical figures given above. Hill, on the other hand, isolated a somewhat similar red colouring matter, nycanthin, from the flowers of the *Nycanthes arbor tristis* (Trans., 1907, **91**, 1501), of approximately the same composition ($C = 72·67$; $H = 8·24$), but his melting point, namely, 234—235°, was much lower than that given by the red colouring matter of the *Cedrela toona*.

Being in possession of a small amount (47 grams) of an old sample of the flowers of the *Nycanthes arbor tristis*, this was examined according to Hill's method in the hope of preparing sufficient nycanthin for purposes of comparison. The product obtained by the action of acid on the hot aqueous extract, which extract, curiously enough, possessed an aromatic odour very similar, if not identical, to that of an infusion of the Toon flowers, was but small in amount, but of a bright red colour, and this when collected, dried, and extracted with hot alcohol left merely a trace of a brown residue similar to that described above (*C*). From the extract by processes already given, 0·09 gram of crude nycanthin was eventually isolated, and this was crystallised from a trace of pyridine. The appearance and general properties of the pure substance were identical with those of the red colouring matter of the *Cedrela toona*, and experiment showed that not only its melting point, but a melting point of a mixture of the two substances, was 285—287°. This colouring matter from the *Cedrela toona* is thus nycanthin, and the melting point given in Hill's paper is incorrect and possibly a misprint.

The small amount of pure nycanthin available (1 gram approx.) did not permit, after analytical requirements were satisfied, of more than qualitative experiment. Addition of zinc dust to its hot alkaline solution causes decolorisation of the liquid, from which by acidification a colourless or faintly yellow precipitate separates, and this property, according to Zwick (*Ber.*, 1897, **30**, 1972), is also possessed by bixin. Interesting again is the effect of light on the red crystals of nycanthin, for in a few weeks' time these become superficially colourless, a reduction process thus apparently taking place.

The properties assigned to bixin are so generally similar to those of nycanthin that a strong probability exists that the two are closely related, although, on the other hand, it does not seem possible to assign to the latter a formula harmonising with that at present given to bixin ($C_{28}H_{34}O_5$). Hill (*loc. cit.*) suggests two formulæ for nycanthin, namely, $C_{15}H_{20}O_3$ and $C_{20}H_{27}O_4$, the latter being preferred, although the somewhat lower hydrogen values obtained during this investigation point more closely to $C_{15}H_{18}O_3$ or $C_{20}H_{26}O_4$. With respect to the former of these, the older formula of Stein (*J. pr. Chem.*, 1867, **102**, 175) for bixin, namely, $C_{15}H_{18}O_4$, is, however, interesting, as suggesting that bixin may be an hydroxynycanthin, and it seems possible as the result of further work with both colouring matters that some simple relationship of this character will be found to exist between them.

Nycanthin is not a mordant dyestuff, and owing to its insolubility in boiling water cannot be applied to fabrics by the ordinary methods. Such is the case also with bixin, and it was interesting to determine if the somewhat peculiar method which is serviceable for dyeing in the case of the latter, is also applicable to the former colouring matter. This proved to be so, for on immersing cotton in a boiling dilute solution of nycanthin in sodium carbonate for fifteen minutes, and subsequently rinsing the material in acidified water, the orange shade indistinguishable from that given by annatto itself was produced, a fact affording further evidence of the closely allied nature of these two colouring matters.

The final alcoholic mother liquor (*C*) obtained during the isolation of the nycanthin gave on treatment with water an orange, resinous product, which on examination proved to contain a fair amount of a yellow, mordant dyestuff. The isolation of this compound from the accompanying impurities, which consisted of traces of nycanthin, an orange-brown, amorphous substance, and a waxy acid, presented considerable difficulty, and the tedious operations necessary for this purpose need not be described, as simpler methods for its preparation from the flowers were devised.

It was present in minute amount in the aqueous filtrate (*A*), and could be removed from this by means of ether, but it was more satisfactory to employ in the first place an extract obtained by macerating the flowers with cold water The extract digested with

2 per cent. hydrochloric acid at 80° for several hours gave on keeping a brown precipitate, from which by extraction with hot alcohol concentration and a precipitation of the impurities by ether as in the isolation of nycanthin previously given, the yellow dye could be prepared almost free from the secondary substances described above.

Acetylation yielded colourless needles melting somewhat indefinitely, but by repeated crystallisation from alcohol and acetic acid the main constituent melting at 191—195° was obtained. (Found, C=58·52; H=4·46. Calc., C=58·59; H=3·91 per cent.)

It consisted of acetylquercetin, $C_{15}H_5O_7(C_2H_3O)_5$, as was evident from a mixed melting-point determination, and the examination of the properties of the free colouring matter itself.

The more soluble portion of the acetylated product yielded two fractions, melting respectively at 143—152° and 132—135°, but in too meagre amount for satisfactory examination. Analysis of the mixture gave C=59·15; H=4·50, whereas a methoxyl determination was carried out with negative result, and from this it appears possible that in addition to acetylquercetin the acetyl compound of a second flavone colouring matter, $C_{15}H_{10}O_6$, was present.

Experiment indicated that no yellow dyestuffs of this character are present in the flowers of *Nycanthes arbor tristis.*

The brown, amorphous product (*B*) obtained during the isolation of the nycanthin, and which appeared to be identical with that given in much smaller amount by flowers of the *Nycanthes arbor tristis*, was insoluble in the usual solvents, gave on fusion with alkali, phloroglucinol and an acid resembling protocatechuic acid, and possessed the general characteristics of the phlobaphens, which are produced when the so-called catechol tannins (phlobotannins) or their glucosides are digested with hot dilute acid. A tannin analysis of the Toon flowers, carried out by Mr. H. Brumwell, of the Leather Industries Department of this University, gave the tannin absorbed by hide as 2·10 per cent., a slightly lower result than was to be expected by the weight of the phlobaphen actually obtained. As catechins also yield phlobaphens, an attempt was made to isolate a compound of this character by agitating a concentrated extract of the flowers with ethyl acetate, but with negative result, although the presence of a tannin or catechin glucoside in the aqueous liquid is not thus precluded. The ethyl acetate extract on evaporation yielded an orange-yellow syrup, and this when digested with boiling dilute acid gave a crystalline precipitate of the mixed yellow colouring matters previously discussed, but no trace of phlobaphen.

In addition to the above-described compounds a small amount of a crystalline sugar, at present unidentified, was isolated, this being deposited as a viscous mass contaminated with plant wax when a concentrated alcoholic solution of the flowers was allowed to remain for some days in cold weather. After removal of wax, it separated from its solution in absolute alcohol on long keeping in nodules, and by recrystallisation from 95 per cent. alcohol was obtained in prisms extremely soluble in cold water. It melted at 165—168°, a point almost identical with that given by mannitol, $C_6H_{14}O_6$, which, curiously enough, was isolated by Hill from the flowers of *Nycanthes arbor tristis*, but analysis indicated that it could hardly be identical with this compound.

Found: $C = 41·85$; $H = 6·06$.

$C_{12}H_{22}O_{11}$ requires $C = 42·11$; $H = 6·43$ per cent.

Dyeing Properties.

Cotton and woollen fabrics can be dyed a dull yellow colour by mere immersion in a boiling extract of the flowers of *Cedrela toona*. This is, however, not permanent, and is removed, although much more quickly from the cotton, by the action of soap or dilute alkali. Better results are, however, obtained by the action of mordants, and the following shades were obtained with mordanted woollen cloth:

Chromium.	Aluminium.	Tin.	Iron.
Dull brownish-yellow	Full golden-yellow	Bright yellow	Dull olive-brown

The yellow produced on wool without the aid of a mordant can be rendered permanent, although duller, by an after treatment with boiling potassium dichromate (3 per cent. on the weight of wool) solution. It was not possible, however, to confirm the statement of Wardle (*loc. cit.*) as to the existence of a large quantity of yellow colouring matter in these flowers, for to obtain a fairly deep shade with the sample employed, a weight of the material at least equivalent to that of the wool was necessary in the dyeing process. During the operations described, nycanthin or its glucoside apparently plays no part, and although experiments were carried out with the object of obtaining the orange-red shade given with nycanthin by means of the flowers themselves, these have hitherto been unsuccessful. On the other hand, if by means of a suitable ferment the nycanthin glucoside was hydrolysed, the dyeing effect would be but feeble, owing to the minute quantity of colouring matter thus liberated. Possibly the seeds of this plant, which are stated to yield a red dye, may give better results, and these will be examined as soon as opportunity occurs.

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CLXVI.—*Electrolytic Reduction. Part VII. The Catalytic Action of Copper.*

By Herbert Drake Law.

It has already been placed on record (Trans., 1912, **102**, 1024) that citral yielded a readily volatile portion when reduced electrolytically in an acid medium. The quantity of the fraction of low boiling point varied considerably in different experiments, and amounted to 90 per cent. of the total reduction product in certain cases. The largest yield was obtained when copper cathodes were employed, and at the same time the hydrogen absorption was greatest. This was quite contrary to past experience with aromatic compounds, and seemed worthy of further investigation. It was soon discovered that the course of the reaction varied most with copper cathodes, and hardly at all with lead. Massive copper was least active, whereas thin sheets gave good yields of highly reduced products. Thick sheet copper, which had been etched with concentrated nitric acid to a fine state of division, was extremely active; but the best results were obtained by depositing finely divided metal, during reduction, on to cathodes of copper foil. Both the rate and the amount of hydrogen absorbed increased with the activity of the metal. Similar experiments were also tried with other aldehydes and ketones, and many were found to behave like citral. All aliphatic and alicyclic compounds containing an unsaturated carbon atom and a carbonyl group in the conjugated position resembled citral. Saturated and unsaturated ketones and aldehydes not included in the above class behaved like benzaldehyde, and were most readily attacked by hydrogen evolved from surfaces of high supertension.

A further peculiarity was noticed with the substances of the citral class: they all readily formed compounds with the lead of the cathodes during reduction, and yielded heavy, fairly stable, red oils containing considerable quantities of the combined metal. The members of the other class did not generally behave in this manner in the following experiments. The aromatic compounds invariably left the lead cathode quite unattacked, and the remaining members reacted in a similar manner, or yielded only very small quantities of the metallic compound. The formation of lead compounds has already been investigated by Tafel (*Ber.*, 1911, **44**, 323), but under different conditions, and no comparison can be made.

EXPERIMENTAL.

Small scale experiments, in which not more than 10 grams of substance was reduced at a time, were conducted in the apparatus already described (Trans., 1909, **89**, 1512). Larger quantities of material were frequently treated, and a useful modified procedure was introduced. The cathode and anode compartments were interchanged. The cathode was the usual flag electrode, bent into the form of a cylinder, and fixed into a rubber stopper with sealing-wax. A porous pot of small diameter also passed through the rubber stopper, and served as an anode compartment. An exit for the evolved hydrogen was also provided. This apparatus was frequently used, as the progress of the reaction could be kept under strict observation, and the cathode solution could be easily maintained at a constant temperature. The solvent used throughout the following experiments was absolute alcohol. The electrolyte was sulphuric acid or potassium hydroxide, in the form of a 5 per cent. solution of the total volume of liquid. The electrodes were sheet lead or electrolytic copper foil. A small quantity of copper sulphate crystals were added to the cathode solution when copper electrodes were used. This caused a slow deposition of copper in a flocculent and finely divided state on the cathode, and exerted a powerful catalytic action.

Mesityl Oxide.

Many preliminary experiments were conducted with mesityl oxide. The cathode solution contained 5 grams of mesityl oxide, 25 c.c. of alcohol, 50 c.c. of water, and 5 per cent. of sulphuric acid or potassium hydroxide. Many forms of copper electrodes were tried in acid media. These were usually cut from commercial sheet copper, and measured from 0·5 to 0·7 mm. in thickness. The reaction was very irregular, and it was soon found that some electrodes were far more active than others. The activity of these electrodes diminished gradually after being used for several experiments without cleaning, but recovered by dipping into concentrated nitric acid. All electrodes which had worn thin by continual cleaning greatly increased in activity. The copper used in the final experiments was cut from foil made from the electrolytic metal, and varying in thickness between 0·05 and 0·1 mm. This was cleaned by dipping into concentrated nitric acid, and washed in cold water. A piece of very fine copper gauze soldered to a stout wire was also tried in some of the later experiments. The best results were obtained with the copper foil, especially if 0·5 gram of copper sulphate crystals were added to the cathode solution, in order to keep the surface of the metal freshly deposited as long as possible. The following results were obtained in a comparative series, using sulphuric acid as electrolyte:

Cathode material.	Lead.	Copper.	Copper.	Copper.	Copper.
Thickness of cathode	2 mm.	0·7 mm.	0·5 mm.	0·06 mm.	0·07 mm.
Copper sulphate addition	none	none	none	none	0·5 gram.
Hydrogen absorbed in 4 hours........................	750 c.c.	900 c.c.	700 c.c.	900 c.c.	1000 c.c.

A similar set of experiments was also conducted in alkaline solution with a sheet lead and a copper foil cathode. The absorption was then equivalent to 700 c.c. and 600 c.c. of hydrogen respectively in four hours' time.

The constituents of the reduction product varied very considerably in different experiments. Increased activity of the cathode caused a diminution in the percentage of the fraction of high boiling point; thus the best yield of deoxymesityl oxide was obtained in alkaline solution on copper cathodes, whereas the largest quantity of readily volatile product was produced in an acid medium and an electrode of copper foil. The former experiments yielded 70 per cent. of the fraction of high boiling point, but the latter only 3—4 per cent. The readily volatile portion was examined in detail in the following experiments. A solution of 50 grams of mesityl oxide, 50 c.c. of sulphuric acid (10 per cent.), 100 c.c. of water, 100 c.c. of alcohol, and 2·5 grams of copper sulphate crystals were reduced in the bottle previously described. The apparatus was cooled in a stream of cold water. A current of 3 amperes was passed through the mixture for ten hours, which was insufficient for complete reduction. The cathode had an area of 75 sq. cm. on one side. The product had separated into two layers, which were carefully removed and treated alone. The top layer was washed with small quantities of water, dried, and fractionated. The above washings were added to the lower layer, and the mixture was distilled over a small flame to remove the alcohol, which was then used as the solvent for the next reduction. This procedure was not absolutely necessary, but it was found to be a useful method of accumulating workable quantities of product dissolved in the aqueous alcoholic portion.

The final alcoholic distillate was washed, dried, and fractionated as above. Altogether, 280 grams of mesityl oxide were reduced, and the following mixed fractions were obtained:

(I.) B.p. 58—71°, 61 grams. (II.) B.p. 72—100°, 16 grams.
(III.) B.p. 105—140°, 140 grams. (IV.) B.p. above 140°, 15 grams.

Each fraction was washed with water to remove the last trace of alcohol, dried, and redistilled.

(I) boiled chiefly at 57—67° in two portions of equal quantities above and below 62°. Both these were mixtures, and contained unsaturated hydrocarbons. The portion of lower boiling point was obtained later in a pure state, as will be described below. The fraction of higher boiling point was probably composed chiefly of *iso*hexylene, $CMe_2{:}C{:}CH{\cdot}CH_2Me$, with which it corresponded in all respects. The corresponding *iso*hexane may also have been present, but the quantity was too small to isolate.

Fraction (II) was a mixture of (I) and (III), and need not be further considered. Fraction (III) was split up into two main portions, boiling respectively at 115—120° and 120—124° in approximately equal quantities. These were both treated in the same manner, and were heated on the water-bath for several hours with four times their volume of dilute sulphuric acid. The distillate was collected, washed with water, dried, and fractionated, when 10 grams of a saturated hydrocarbon were obtained, boiling at 57—58°. This substance corresponded in all respects with the hexane, $CHMe_2{\cdot}CHMe_2$, which was probably present in the fraction of low boiling point mentioned above. The washings of this hydrocarbon contained considerable quantities of acetone (semicarbazone, m. p. 180°), which was evidently one of the decomposition products of hydrolysis. It seemed probable, therefore, that mesityl oxide had been reduced partly according to the following equation:

$$2CMe_2{:}CH{\cdot}COMe + 6H = CMe_2{:}CH{\cdot}CHMe{\cdot}CHMe{\cdot}CH{:}CMe_2 + 2H_2O.$$

This complex hydrocarbon then became hydrolysed progressively by the sulphuric acid of the electrolytic mixture, and the subsequent treatment on the water-bath:

$$(1)\ CMe_2{:}CH{\cdot}CHMe{\cdot}CHMe{\cdot}CH{:}CMe_2 + H_2O = CMe_2{:}CH{\cdot}CHMe{\cdot}CHMe_2 + Me_2CO.$$

$$(2)\ CMe_2{:}CH{\cdot}CHMe{\cdot}CHMe_2 + H_2O = CMe_2{:}CH{\cdot}CH{:}CMe_2 + Me_2CO.$$

The above reaction is similar to the formation of dibenzyl from benzaldehyde. It should be remarked, however, that the amount of acetone produced by hydrolysis was in excess of that required by the above equation, and was produced in all probability from unchanged mesityl oxide. The flask on the water-bath still contained considerable quantities of an unattacked oil. This was removed and shaken with a saturated solution of sodium hydrogen sulphite, when a white, crystalline compound was deposited, from which methyl *iso*butyl ketone was isolated. It boiled at 116—117°, and formed a semicarbazone melting at 132°. The two portions mentioned above yielded the same products, but that of higher boiling point contained appreciably larger quantities of unchanged mesityl oxide, which was detected in the increased yield of acetone on hydrolysis. The unsaturated alcohol *iso*hexenol was not isolated, but its presence was suspected in these fractions.

Fraction (IV) consisted chiefly of unchanged mesityl oxide and a small quantity of deoxymesityl oxide.

Citral.

A large number of comparative experiments were conducted with citral. Twenty-five grams of citral, 150 c.c. of alcohol, 50 c.c. of $4N$-sulphuric acid were treated at the same time in a duplicate experiment. The cathode measured 75 sq. cm. on one side. A current of 2 amperes was employed for ten hours (overnight). The products from 50 grams of material were distilled in a current of steam, with the following results:

1. Material of cathode.	2. Weight of copper sulphate added to cathode solution.	Weight of volatile product.
Sheet lead (10 mm.)	none	7·5 grams
Sheet copper (0·7 mm.).........	none	10 ,,
Copper foil (0·06 mm.)	none	27 ,,
Copper foil (0·06 mm)	1 gram	45 ,,

The last experiment contained an addition of 1 gram of copper sulphate crystals dissolved in the cathode solution. The volatile product was similar in all cases, and contained chiefly the mixture of geraniols already described (*loc. cit.*).

Pulegone.

A mixture containing 15 grams of pulegone, 40 c.c. of sulphuric acid (10 per cent.), and 60 c.c. of alcohol was reduced, employing a current of 2 amperes for six hours. Two experiments were conducted, using sheet lead and copper foil as cathodes. The superficial area was 75 sq. cm. in both cases. One gram of copper sulphate was dissolved in the cathode solution when copper foil was used as electrode.

The product was diluted with water, extracted with ether, dried, and fractionated. It was noticeable that the usual lead compound was formed as a heavy, red, insoluble oil in the first experiment, and the lead cathode was considerably etched. The product boiled chiefly at 202—207°, and was menthone; but there was also present a fraction of higher boiling point. The yield of menthone was 95—100 per cent. with the copper cathode, and 50—60 per cent.

with the lead. The residue in the latter case was a complex lead containing red oil.

Carvone.

Twenty grams of carvone, 100 c.c. of alcohol, 100 c.c. of dilute sulphuric acid, and 2 grams of copper sulphate were dissolved and reduced with a current of 2 amperes for four hours. The cathode was copper foil, measuring 75 sq. cm. on one side. The product was diluted with water, and treated in the usual manner. The oil boiled at 218—222° with practically no residue, and was composed almost entirely of dihydrocarvone.

Many of the above results did not agree with those already recorded for aromatic compounds. It has been shown in several papers (*loc. cit.*) that the benzene derivatives are most readily attacked when reduced in the presence of metals of the highest supertension. Only one record has been made (Trans., 1906, **89**, 1524) of an exception to this rule, and this experiment has not been successfully repeated. The result was probably accidental, but further work will be undertaken to reproduce the correct conditions. It seemed of interest to conduct reduction experiments on closely allied compounds in order to determine the connexion between the rate of reduction and chemical constitution. This was carried out, and the results are given in the table below. Each reduction was conducted at ordinary temperature with 5 grams of substance, except in the last example, where 10 grams were used at a temperature of 50°. A set of three experiments was conducted in series, one with a sheet lead cathode, the second with copper foil, and the third as a blank, to which no reducible material was added. This series was repeated several times in most cases, and the product was sometimes extracted and examined. 0·5 Gram of copper sulphate dissolved in a small quantity of water was always added when copper foil was employed as cathode, but due allowance was made for this on recording the hydrogen absorption due to reduction. The compounds bracketed are closely allied in constitution, and differ only in respect to the unsaturated linking.

The second and third columns show the amount of hydrogen absorbed on lead and copper cathodes respectively, and the fourth column shows the result for no absorption at all.

The time of each experiment varied somewhat on account of convenience, but no experiment was stopped until the rate of hydrogen absorption had diminished almost to nothing.

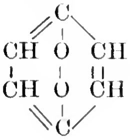
The following table shows that the $\alpha\beta$-unsaturated aldehydes and ketones of the aliphatic and alicyclic series are more reducible in the presence of finely divided copper than with sheet lead. This

	Hydrogen absorbed with electrodes.		
Compound reduced.	1. Sheet lead.	2. Copper foil.	3. Blank.
Mesityl oxide	700 c.c.	800 c.c.	1400 c.c.
Methyl *iso*butyl ketone	350	200	2000
Citral	650	1000	1500
Citronellal	140	0	1800
Methylheptenone (natural)	750	0	1200
Dimethylmesityl oxide	780	850	1600
Pulegone	570	650	1590
Menthone	450	80	1600
Carvone	650	800	1330
Dihydrocarvone	300	0	1300
Cinnamaldehyde	950	490	1030
Benzil	830	600	1570
p-Benzoquinone	790	780	1650
Crotonaldehyde	620	700	1000
Butaldehyde	390	130	1010
Styryl methyl ketone (10 grams)	1240 (50°)	850 (50°)	1600

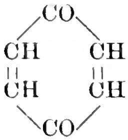
property was quite characteristic for copper, and no similar catalytic action was observed with any form of lead. The nature of the reaction was quite different, however, with the two metals in question. The product of the lead cathode always contained considerable quantities of a heavy, red oil. This substance was a combination of the partly reduced carbonyl compound and the lead of the cathode. The exact nature was not closely studied.

The formation of these insoluble lead salts probably accounted for the relatively slow rate of reduction. They were obtained in appreciable quantities only from the αβ-unsaturated aldehydes and ketones, as previously stated. The carbonyl compounds of the aromatic series did not yield the least trace of these lead compounds, and the saturated aldehydes and ketones only small quantities. The reaction appeared to be characteristic of the aliphatic and alicyclic series, and is suggested as a test for αβ-unsaturation of carbonyl compounds of these groups.

It seemed of interest to investigate the nature of the quinones according to the above relations. The constitution of these substances is still open to some doubt, but is generally accepted as one of the following:



(I.)



(II.)

(I) represents a peroxide of the aromatic series, which, on electrolytic reduction, should partly produce resins. The rate of reduction would be greatest on lead cathodes, and the resin formation least.

Compound (II) is obviously derived from an alicyclic unsaturated ketone, and should produce little or no resin on reduction. Reduction might take place at the carbonyl groups, the unsaturated linkings, or at both. Experience shows that only the ketone groups are attacked with the formation of a hydroxyl compound of the aromatic series. The latter fact excludes the possibility of the formation of lead salts, which are never produced with aromatic compounds. It was anticipated, therefore, that *p*-benzoquinone would resemble pulegone and carvone in its behaviour towards electrolytic hydrogen, with the exception of the formation of compounds with the lead of the electrodes. The following are some of the results recorded:

p-Benzoquinone reduced, grams.	Cathode material.	Copper sulphate. grams.	Hydrogen absorbed in c.c.	Control in c.c.
5	Copper foil	0·0	870	1770
5	,, ,,	0·5	880	1770
5	,, ,,	1·0	880	1770
5	Copper gauze	0·5	870	1820
5	Lead sheet	0·0	820	1820
5	Copper gauze	0·0	1060	1640
5	Lead sheet	0·0	1060	1640
3	Copper gauze	0·0	600	1800
3	Lead sheet	0·0	550	1800

The quantity of material reduced at one time usually amounted to 5 grams. The *p*-benzoquinone was dissolved in a mixture of alcohol and ethyl acetate, and added to the requisite quantity of dilute sulphuric acid and copper sulphate solution. The cathodes measured 20 sq. cm. on one surface, and the current was maintained at 1 ampere throughout. The first product of reduction was quinhydrone, which frequently separated from solution in lustrous, greenish-brown crystals of metallic appearance. The formation of this insoluble intermediate product led to considerable irregularity in the results, and comparison is admissible only in experiments of the same series (bracketed). Even in these cases a small amount of local heating was liable to arise and affect materially the rate of reduction. The last two experiments were conducted with smaller quantities of *p*-benzoquinone to avoid this difficulty, and it was expected that no separation would take place. This anticipation was fulfilled, but did not greatly alter the comparative rates of reduction. There is a second consideration with respect to quinhydrone which should not be overlooked. This substance, according to the generally accepted formula, is no longer a ketone, and certainly not an unsaturated ketone. It is, however, an unstable combination in solution, and probably dissociates into quinol and *p*-benzoquinone. Further reduction was probably due to the presence of the dissociated quinone, and not to the dissolved intermediate formation.

An attempt was next made to reduce pulegone on lead cathodes without the formation of the metallic compound. It was thus hoped to obtain results comparable to those of *p*-benzoquinone. This was accomplished by using sheet lead which had not been cleaned with concentrated nitric acid. It was then found that the metal sometimes remained unattacked throughout a considerable part of the experiment. The amount of hydrogen absorbed was then practically the same on both copper and lead, and amounted to 665 c.c. and 670 c.c., for the complete reduction of 5 grams of pulegone. It appears, therefore, that *p*-benzoquinone has the properties of an $\alpha\beta$-unsaturated ketone, which, however, forms an aromatic reduction product.

In conclusion, I wish to express my thanks to the Government Grant Committee for partly defraying the cost of this work.

CLXVII.—*Nitrites of the Mercurialkyl- and Mercurialkylaryl-ammonium Series. Part II.*

By Prafulla Chandra Rây, Nilratan Dhar, and Tincowry De.

Mercurihexamethylenetetra-ammonium Nitrite, $(CH_2)_6N_4,Hg(NO_2)_2$.

This salt was prepared in the usual manner, namely, by the interaction of an aqueous solution of mercuric nitrite and hexamethylenetetramine; as the salt is fairly soluble in water, concentrated solutions of the components were used. The salt was obtained as a dirty white, crystalline powder.

Found: Hg = 44·50; C = 16·50; N = 20·04.

$C_6H_{12}N_4,Hg(NO_2)_2$ requires Hg = 46·30; C = 16·67; N = 19·44 per cent.

Mercuriethylenediammonium Nitrite, $C_2H_4(NH_2)_2,Hg(NO_2)_2$.

A dilute solution of ethylenediamine (b. p. 116·5°) was added to a dilute solution of mercuric nitrite. A white precipitate of a granular character was immediately formed. The composition of this substance was found to vary in successive preparations, and no definite formula could be assigned to it. The filtrate, which had a distinct odour of the free amine, was allowed to remain overnight, and a scaly, lustrous, pale brownish-yellow, crystalline precipitate was formed on the sides and bottom of the beaker. The precipitate was dried in a steam-oven, and analysis showed that it corresponded with the formula $C_2H_4(NH_2)_2,Hg(NO_2)_2$.

Found: Hg=(I) 55·0, (II) 56·13, (III) 57·9; C=(I) 6·7; N=(I) 16·39, (II) 15·35.

$C_2H_8N_2,Hg(NO_2)_2$ requires Hg=56·82; C=6·82; N=15·91 per cent.

Both the above salts dissolved readily in hydrochloric acid with copious evolution of nitrous fumes. In a previous communication (this vol., p. 616) all the members of this series were provisionally regarded as additive compounds. It has lately been found, however, that most of these are appreciably soluble in water; and it therefore occurred to us that the measurement of their conductivity might throw light on their constitution. Owing, however, to the wide divergence in the range of their solubilities, the conductivity measurements could not be taken under similar dilutions. It will, however, be noticed on reference to the tables given below that fairly comparable numbers are obtained; for example, the molecular conductivity of the diphenyl and the dibenzylethyl salts at a dilution of about 1000 litres are nearly 100 in ordinary units.

(1) *Mercuribenzylmethylammonium Nitrite*, $2(NHMe\cdot C_7H_7),Hg(NO_2)_2$.

Molecular conductivity.	Dilution in litres.	Equivalent conductivity.	Dilution in litres.
86·40	1265	43·20	632·5
98·92	3795	49·46	1897·5
100·69	11385	50·34	5692·5

(2) *Mercuribenzylammonium Nitrite*, $NH_2\cdot C_7H_7,Hg(NO_2)_2,H_2O$.

Molecular conductivity.	Dilution in litres.	Equivalent conductivity.	Dilution in litres.
151·30	2557·7	75·65	1278·85
152·10	7673·1	76·05	3836·55
153·15	23019·3	76·57	11509·65

(3) *Mercuribenzylethylammonium Nitrite*, $2(NHEt\cdot C_7H_7),Hg(NO_2)_2$.

Molecular conductivity.	Dilution in litres.	Equivalent conductivity.	Dilution in litres.
100·15	890	50·07	445
105·37	2670	52·68	1335
108·58	8010	54·29	4005

(4) *Mercuriphenylammonium Nitrite*, $2NH_2Ph,Hg(NO_2)_2,H_2O$.

Molecular conductivity.	Dilution in litres.	Equivalent conductivity.	Dilution in litres.
109·09	1180·2	54·54	590·1
158·36	3540·6	79·18	1770·3
259·49	10621·8	129·74	5310·9
260·00	31865·4	130·00	15932·7

(5) *Mercuri*iso*butylammonium Nitrite*, $2NH_2 \cdot C_4H_9,3Hg(NO_2)_2$.

Molecular conductivity.	Dilution in litres.	Equivalent conductivity.	Dilution in litres.
381·21	3636	63·53	606
401·46	10908	66·91	1818
402·52	32724	67·08	5454

The *iso*butylamine salt which has been described in a previous paper had the formula $NH_2 \cdot C_4H_9,Hg(NO_2)_2$.

Found: Hg = 58·53.

$C_8H_{20}N,3Hg(NO_2)_2$ requires Hg = 58·70 per cent.

(6) *Mercuriethylenediammonium Nitrite*, $C_2H_4(NH_2)_2,Hg(NO_2)_2$.

Molecular conductivity.	Dilution in litres.	Equivalent conductivity.	Dilution in litres.
142·32	302·6	71·16	151·3
261·66	907·8	130·83	453·9
378·67	2723·4	189·33	1361·7
410·94	8170·2	205·47	4085·1
439·41	24510·6	219·17	12255·3

(7) *Mercuripiperazinium Nitrite*, $C_4H_{10}N_2,Hg(NO_2)_2$.

Molecular conductivity.	Dilution in litres.	Equivalent conductivity.	Dilution in litres.
260·89	711·5	130·44	355·75
329·55	2134·5	164·77	1067·25
391·77	6403·5	195·88	3201·75
431·07	18210·5	215·53	9105·25
432·01	54631·5	216·00	27315·75

(8) *Dimercuriammonium Nitrite*, $NHg_2NO_2,\frac{1}{2}H_2O$ (Trans., 1902, **81**, 645).

Molecular conductivity.	Dilution in litres.	Equivalent conductivity.	Dilution in litres.
317	6390	79·25	1597·5
466	19170	116·50	4792·5
542	57510	135·50	14377·5

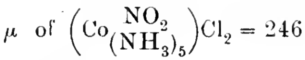
(9) *Mercurihexamethylenetetra-ammonium Nitrite*, $(CH_2)_6N_4,Hg(NO_2)_2$.

Molecular conductivity.	Dilution in litres.	Equivalent conductivity.	Dilution in litres.
104·3	1296	52·15	648
150·8	3888	75·40	1944
206·7	11664	103·35	5832

In these experiments the temperature was 30°, and the "conductivity" water was specially purified.

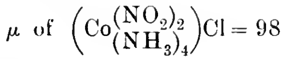
Discussion of Results.

From the above tables it is evident that the molecular conductivities of the monoamine salts are almost equal to those of ammonium nitrite and alkali metal nitrites under the same conditions (that is, about 100 at a dilution of 1000 litres), whilst the molecular conductivities of the salts obtained from ethylenediamine and piperazine (di-acid amines) are equal to those of the alkaline earth nitrites (that is, about 250 at a dilution of 1000 litres). Werner and Miolati (*Zeitsch. physikal. Chem.*, 1893, **12**, 35; 1894, **14**, 506) from electrical conductivity measurements of complex amine compounds of metals have shown that when there are two ions in solution the molecular conductivity of the salt becomes 100 at a dilution of 1000; and when there are three ions it becomes nearly 250 under similar conditions, as, for example,



$$\mu \text{ of } \left(\mathrm{Co}{}^{\mathrm{NO}_2}_{(\mathrm{NH}_3)_5}\right)\mathrm{Cl}_2 = 246$$

at a dilution of 1000 litres,



$$\mu \text{ of } \left(\mathrm{Co}{}^{(\mathrm{NO}_2)_2}_{(\mathrm{NH}_3)_4}\right)\mathrm{Cl} = 98$$

under similar conditions.

From the tables it is seen that these mercury compounds, with the exception of piperazine and diamine compounds, give only two ions in solution, since the molecular conductivities at a dilution of about 1000 litres are nearly 100, whilst those of the piperazine and ethylenediamine salts under similar conditions are about 250. It appears, therefore, that the last-named salts yield three ions. Moreover, it has been found that strong bases cannot precipitate dimercurion ($Hg^{\cdot\cdot}$) from the salts as HgO, or rather $Hg(OH)_2$, proving the existence of mercury as part of a complex ion. Ley and Schaefer (*Ber.*, 1902, **35**, 1309) have shown that aqueous solutions of mercuric derivatives of amides, imides, and similarly constituted compounds do not give the reactions of dimercurion, the mercury always forming a complex ion.

Heilwig (*Zeitsch. anorg. Chem.*, 1900, **25**, 157) has investigated the products resulting from the addition of silver nitrate to the halogen salts of silver, and has shown that they contain the complex radicles, $IAg_3^{\cdot\cdot}$, $IAg_2^{\cdot}$, $BrAg_2^{\cdot}$, etc.; he also succeeded in obtaining solid salts which gave these ions in solution.

In the different varieties of mercury compounds containing nitrogen prepared by Adams (*Amer. Chem. J.*, 1902, **28**, 198), Piccininni and Ruspaggiari (*Gazzetta*, 1892, **22**, ii, 604), Hoffmann and Marburg (*Annalen*, 1899, **305**, 191; *Ber.*, 1897, **30**, 219), mercury always forms a part of a complex radicle.

In the series described by us, dilute acids liberate nitrous acid from all the members; thus, nitrosion (NO_2) exists in the free state in all these salts. From these facts it is evident that mercury forms the part of a complex positive ion, while the negative ion is the nitrosion. In the di-acid-amine salts the two NO_2-groups exist as negative ions, thus behaving exactly like the alkaline earth nitrites. In the monoamine salts, only one NO_2-group behaves as ion; thus, for example, in the case of mercuribenzylammonium nitrite, the positive ion is $[C_6H_5{\cdot}CH_2{\cdot}NH_2{\cdot}HgNO_2]$, and the negative ion is NO_2. When diacids are introduced into a solution of this salt, undissociated nitrous acid is formed, which instantly decomposes; thus the ionic equilibrium is disturbed by the introduction of acids; the salt dissolves completely with evolution of nitrous fumes. Adopting Werner's view in the case of the diacid-amine salts, the two NO_2-groups are indirectly connected with mercury; thus, $[C_2H_4(NH_2)_2Hg](NO_2)_2$ is the formula of the ethylenediamine salt. In the case of the monoamine salts, however, one NO_2-group is linked directly to the mercury atom, whilst the other is indirectly attached (compare also Jörgensen, *Zeitsch. anorg. Chem.*, 1897, **14**, 410).

Thus, $[C_6H_5{\cdot}CH_2{\cdot}NH_2{\cdot}HgNO_2]NO_2$ is the formula of mercuribenzylammonium nitrite. In this, however, the direct linking of the NO_2-group is not quite as stable as in those described by Werner (compare "New Ideas on Inorganic Chemistry," English translation by Hedley, pp. 39–43).

If we compare the table of equivalent conductivity * of salts, we see that they are always almost equal except those of piperazine and ethylenediamine, which in themselves quite agree. So dimercuriammonium nitrite, mercuri*iso*butylammonium nitrite, the molecular conductivities of which cannot be brought under comparable results owing to their very sparing solubility, also seem to belong to the same series, since their equivalent conductivities agree with the typical members.

That these substances are not probably additive compounds may be seen from these simple considerations. The sum of the molecular conductivities of the amines (Bredig, *Zeitsch. physikal. Chem.*, 1893, **12**, 294) and mercuric nitrite (this vol., p. 965) falls very much short of the actual molecular conductivities of their salts, as found by experiment. If the amines were in the free state they would, when dissolved in water, yield hydroxydion; but in these salts no test for the presence of the hydroxydion is obtained.

Mercuric nitrite as well as the amines are exceedingly soluble

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* By equivalent conductivity is meant the conductivity of the solution which contains one gram-equivalent of mercury in a litre of the solution.

in water, but the products formed by mixing them are very sparingly soluble. From these arguments it is almost clear that these compounds are not of an additive nature, but are true nitrites with a complex positive ion containing mercury.*

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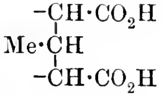
CLXVIII.—*The Chemistry of the Glutaconic Acids. Part V. The Preparation of Esters of the Labile Acids.*

By Norman Bland and Jocelyn Field Thorpe.

Up to the present time four acids of the glutaconic series containing the movable or mobile hydrogen atom have been isolated in two modifications, namely:

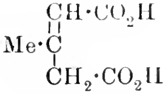
α-Methylglutaconic acid,	m.p.	145—146°	and	118°
α-Ethylglutaconic acid	,,	133—134	,,	108
α-Benzylglutaconic acid	,,	153—154	,,	139
β-Methylglutaconic acid	,,	147	,,	115—116

The experimental evidence recorded in the previous parts of this series has led us to the conclusion that these isomeric acids are not related to one another in the same manner as fumaric and maleic acids, but have a difference in structure due to the position of the tautomeric hydrogen atom within the molecule. Thus the isomerides of lower melting point are regarded as labile acids formed from the hydroxy-anhydrides under conditions which cause the hydrogen atom to come to rest within the carbonyl system; the modifications of higher melting point, on the other hand, are the normal acids similar in structure to *iso*phthalic acid, which are produced under conditions which allow the hydrogen atom to pass into its more stable position within the three-carbon system. In this way the two modifications of, for example, β-methylglutaconic acid can be represented by the formulæ:



$$\begin{array}{l}-CH\cdot CO_2H\\ \quad|\\ Me\cdot CH\\ \quad|\\ -CH\cdot CO_2H\end{array}$$

Normal acid.
M.p. 147°.



$$\begin{array}{l}CH\cdot CO_2H\\ \|\\ Me\cdot C\\ |\\ CH_2\cdot CO_2H\end{array}$$

Labile acid.
M.p. 115—116°.

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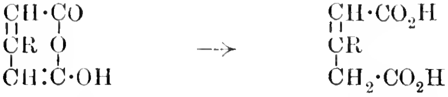
* Hilditch and Smiles have shown that the so-called additive compound of triethylsulphonium iodide with mercuric iodide, $(C_2H_5)_3SI,HgI_2$, can be really regarded as an "atomic" compound, $(C_2H_5)_3SI_2{\cdot}HgI$ (Trans., 1907, **91**, 1395).

Investigation has shown that it is usually possible to isolate the labile forms of the acids by hydrating the hydroxy-anhydrides by strong aqueous alkali or by dilute alkali in the presence of casein, thus:



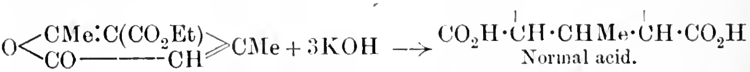
$$\begin{array}{l} CH\cdot CO \\ CR\ \ O \\ CH{:}C\cdot OH \end{array} \longrightarrow \begin{array}{l} CH\cdot CO_2H \\ CR \\ CH_2\cdot CO_2H \end{array}$$

Labile acid.

This method is, however, open to the objection that it is a very difficult matter to prevent the hydrogen atom introduced by the hydration of the hydroxy-anhydride from passing, at the moment of fission of the pyrone ring, into the three-carbon system, and in this way yielding the normal acid. Thus, although it has been shown that the presence of the methyl group in β-methylglutaconic acid confers considerable stability on the labile form of the acid, it is a matter of some difficulty to obtain the labile acid by the hydration of the hydroxy-anhydride.

It seemed to us probable that a general method for the preparation of the labile acids of this type could be found if their open-chain enolic esters, containing a potentially mobile hydrogen atom, were hydrolysed by alkali, and, as a matter of fact, an examination of the literature quickly supplied evidence in favour of this assumption.

During his experiments on the preparation of the two modifications of β-methylglutaconic acid, Feist (*Annalen*, 1906, **345**, 64, 65) discovered the remarkable fact that when ethyl *iso*dehydracetate is hydrolysed by the theoretical amount of alkali, the acid of higher melting point (normal acid) is the sole product:



$$O\!<\!\begin{array}{l} CMe{:}C(CO_2Et) \\ CO\text{———}CH \end{array}\!\!>\!CMe + 3KOH \longrightarrow CO_2H\cdot CH\cdot CHMe\cdot CH\cdot CO_2H$$

Normal acid.

Type (*a*).

$$Me\cdot CO_2H + EtOH$$

whereas the hydrolysis by alkali of the condensation product formed from ethyl tetrolate and ethyl malonate yielded the acid of lower melting point (labile acid) in a pure condition:

$$CMe{:}C\cdot CO_2Et + HCNa(CO_2Et)_2 \longrightarrow$$

$$(CO_2Et)_2C{:}CMe\cdot \overset{*}{C}H{:}C(OH)\cdot ONa\dagger \rightarrow CO_2H\cdot CH{:}CMe\cdot CH_2\cdot CO_2H$$

(I.) Labile acid.

It is evident that the fission of the pyrone ring of ethyl *iso*dehydracetate causes the hydrogen to pass into the three-carbon system. In fact, the analogy between the behaviour of this sub-

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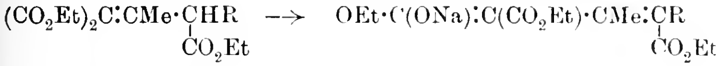
† The reason for assigning this structure to the sodium compound has been given (compare this vol., p. 250).

stance and that of the hydroxy-anhydride is further emphasised by the observation made by Feist that the presence of a large excess of alkali leads to the formation of the acid of lower melting point (labile acid) (compare this vol., p. 866).

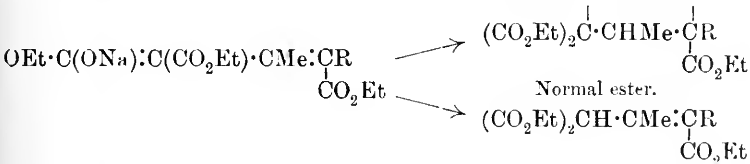
On the other hand, the condensation product (I) of ethyl tetrolate and ethyl sodiomalonate contains a hydrogen atom, marked *, which is potentially the mobile hydrogen atom. The hydrolysis of this ester by alkali gives therefore the labile form of the acid, because the ester retains its structure during hydrolysis, and the hydrogen atom remains within the carbonyl system of the acid.

It is evident that the alkylation of the sodium compound (I) will lead to the production of an ester (II), which, in the form of its sodium derivative, will have the structure (III):



$$\underset{\text{(II.)}}{(CO_2Et)_2C{:}CMe\cdot \underset{\substack{|\\ CO_2Et}}{C}HR} \longrightarrow \underset{\text{(III.)}}{OEt\cdot C(ONa){:}C(CO_2Et)\cdot CMe{:}\underset{\substack{|\\ CO_2Et}}{C}R}$$

This sodium derivative does not contain a potentially mobile hydrogen atom, and it will therefore behave as the corresponding cyano-ester (this vol., p. 878), and give a mixture of the normal and labile esters when the sodium compound is treated with water:

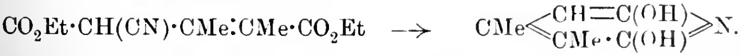


$$OEt\cdot C(ONa){:}C(CO_2Et)\cdot CMe{:}\underset{\substack{|\\ CO_2Et}}{C}R \begin{array}{l} \nearrow (CO_2Et)_2\overset{|}{C}\cdot CHMe\cdot \overset{|}{\underset{\substack{|\\ CO_2Et}}{C}}R \\ \qquad\qquad \text{Normal ester.} \\ \searrow (CO_2Et)_2CH\cdot CMe{:}\underset{\substack{|\\ CO_2Et}}{C}R \\ \qquad\qquad \text{Labile ester.} \end{array}$$

This assumption was verified by experiment; the labile ester (R being methyl) was isolated in the manner previously described for the cyano-ester, and its structure proved by the formation of the labile acid from it on alkaline hydrolysis:

$$(CO_2Et)_2CH\cdot CMe{:}CMe\cdot CO_2Et \longrightarrow CO_2H\cdot CH_2\cdot CMe{:}CMe\cdot CO_2H.$$

This experiment supplied the proof of structure which could not be obtained in the case of the cyano-esters themselves, because these substances are entirely converted into derivatives of 2:6-dihydroxypyridine on alkaline hydrolysis:



$$CO_2Et\cdot CH(CN)\cdot CMe{:}CMe\cdot CO_2Et \longrightarrow CMe{<}\begin{matrix}CH{=}C(OH)\\ CMe\cdot C(OH)\end{matrix}{>}N.$$

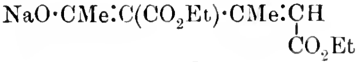
The labile and normal esters of carbethoxy-$\alpha\beta$-dimethylglutaconic acid produced in the above way are analogous to the corresponding cyano-esters. The labile ester is a desmotropic substance, forming equilibrium mixtures of the ketonic and enolic forms at the ordinary temperature. The yield is, however, only about 35 per cent. of the ester converted, and this fact, combined with the tiresome nature of the preparation of ethyl tetrolate caused us to search for some other method by which we could prepare large quantities of the labile esters, since it is our intention in the near future to subject the two types to an extended chemical investigation. Ultimately the following process was found to give the desired result.

Ethyl *iso*dehydracetate (IV) is a substance which can be prepared in large quantities by the action of dry hydrogen chloride on ethyl acetoacetate. We find that the pyrone ring is at once broken by alcoholic sodium ethoxide at 0°, and that a good yield of a yellow sodium compound is obtained from which the corresponding ester can be prepared through the agency of carbon dioxide.

From the fact that this ester gives a pronounced coloration with ferric chloride and is reconverted into the pyrone derivative on distillation, it may be inferred that its structure is represented by formula (V), and that the sodium compound has the formula (VI):

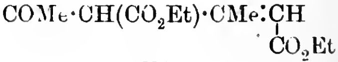
$$O<\begin{array}{l}CMe{:}C(CO_2Et)\\CO\text{———————}CH\end{array}>CMe\ +NaOEt\ \longrightarrow$$

(IV.)



$$NaO\cdot CMe{:}C(CO_2Et)\cdot CMe{:}\underset{\displaystyle CO_2Et}{\underset{|}{CH}}$$

(VI.)



$$COMe\cdot CH(CO_2Et)\cdot CMe{:}\underset{\displaystyle CO_2Et}{\underset{|}{CH}}$$

(V.)

In other words, the presence of the ketonic group causes the hydrogen atom to be retained on the adjacent carbon atom, and renders this substance an exception to the rule given in a previous paper (this vol., p. 250), namely, that derivatives of this type react with sodium ethoxide to form sodium derivatives, which retain the mobile (or potentially mobile) hydrogen atom.

That this is actually the case is at once shown by a comparison of the acetyl ester with the corresponding carboxylic ester (VII), for the first-named, since it does not contain the potentially mobile hydrogen atom, reacts with sodium ethoxide at the ordinary temperature, yielding ethyl acetate and the dicarboxylic ester, whereas the latter, which contains this hydrogen atom, is quite unacted on by sodium ethoxide (compare Trans., 1911, **99**, 192):

$$NaO\cdot CMe{:}C(CO_2Et)\cdot CMe{:}CH\cdot CO_2Et\ +EtOH\ \longrightarrow$$

$$NaO\cdot C(OEt){:}C\overset{*}{H}\cdot CMe{:}CH\cdot CO_2Et\ +CH_3\cdot CO_2Et$$

(VIII.)

$$(CO_2Et)_2C{:}CMe\cdot CH{:}C(OEt)\cdot ONa$$

(VII.)

Moreover, it is evident that the sodium derivative of the dibasic ester (VIII) now contains the potentially mobile hydrogen atom

(*), and that it will react with water, yielding the labile ester (IX) as sole product:

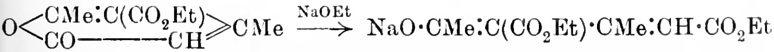
$$\mathrm{NaO\cdot C(OEt){:}C\overset{*}{H}\cdot CMe{:}CH\cdot CO_2Et \longrightarrow \underset{(IX.)}{CO_2Et\cdot CH_2\cdot CMe{:}CH\cdot CO_2Et}}$$

Experiment shows that this is actually the case, and that the labile ester of β-methylglutaconic acid can be prepared in large quantities by this method. The properties of the ester show that it is the pure labile ester. The corresponding ester of the normal acid is best prepared from the normal acid by the aid of alcohol and sulphuric acid; the two isomerides boil at practically the same temperature, but it is hoped that further investigation will reveal important physical and chemical differences.

It is interesting to note that the hydrogen ethyl salts of the two acids are different substances. That from the normal acid melts at 73°, that from the labile acid is a liquid. Since these salts yield their respective acids under the same conditions of alkaline hydrolysis, it is to be concluded that they retain the normal and labile structures.

Having established a method for the preparation of the labile esters of this type, it was clear that we had to hand a means of isolating the labile esters of the corresponding alkyl derivatives substituted on one of the terminal carbon atoms, and it is evident that from these esters the labile forms of the alkyl acids could be prepared.

It is a simple matter to convert ethyl *iso*dehydracetate into the alkylated dicarboxylic ester, for when the pyrone derivative is treated with alcoholic sodium ethoxide and the alkyl iodide at 0°, it is quickly and completely transformed into ethyl acetate and the desired ester:



$$\mathrm{O\Big<\begin{matrix}CMe{:}C(CO_2Et)\\ CO\text{———}CH\end{matrix}\Big>CMe \xrightarrow{NaOEt} NaO\cdot CMe{:}C(CO_2Et)\cdot CMe{:}CH\cdot CO_2Et}$$

$$\mathrm{+\,RI \longrightarrow CO_2Et\cdot CR{:}CMe\cdot CH_2\cdot CO_2Et + NaI + CH_3\cdot CO_2Et.}$$

It is advisable in this reaction to have a slight excess of sodium ethoxide present, but it is certain, both from our experiments as well as from those of Feist and Beyer (*Annalen*, 1906, **345**, 123) that the sodium compounds of the dibasic esters are largely, if not entirely, dissociated in alcohol, and consequently the free sodium ethoxide necessary to effect the elimination of the acetyl group is present throughout the reaction.

It is evident that the dialkylated esters produced in this way are the labile esters, because, since the alkyl group enters on the γ-carbon atom, it follows that the sodium compounds of the esters, which are certainly intermediate products in the reaction, retain a potentially mobile hydrogen (*), and will therefore yield the labile esters:

$$CO_2Et\cdot CR{:}CMe\cdot C\overset{*}{H}{:}C(OEt)\cdot ONa \longrightarrow CO_2Et\cdot CR{:}CMe\cdot CH_2\cdot CO_2Et.$$

It is perhaps desirable to emphasise the fact that probably it is only by such a method as this that the labile esters of the dialkylated esters can be prepared. It might be supposed that this object could be attained by alkylating the dicarboxylic esters. In this case, however, the alkyl group enters on the α-carbon atom yielding the α-alkyl derivative, a condition which we have shown to be unstable:

$$CO_2Et\cdot CH{:}CMe\cdot CH{:}C(OEt)\cdot ONa \longrightarrow CO_2Et\cdot CH{:}CMe\cdot CHR\cdot CO_2Et$$

$$\longrightarrow CO_2Et\cdot \overset{|}{C}H\cdot CHMe\cdot \overset{|}{C}R\cdot CO_2Et.$$

The hydrogen atom therefore passes away from the substituted position towards the more remote carbon atom of the system. To do this it must pass through its most stable position within the three-carbon system, and therefore, as we have proved by experiment, the normal esters are the sole products of reactions of this type (compare this vol., p. 887).

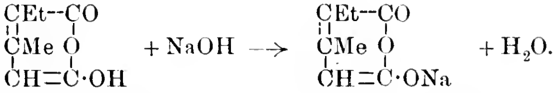
It is, of course, apparent that the labile esters should be produced by the action of water on their sodium derivatives in the manner indicated by the equation given above, but when once the normal esters of this type have been isolated they do not seem to possess any tendency to form sodium derivatives with alcoholic sodium ethoxide (compare *Annalen*, 1906, **345**, 123).

In this way we have therefore been able to prepare the labile esters of both β-methyl-α-ethylglutaconic acid and of $\alpha\beta$-dimethylglutaconic acid, and have prepared the corresponding labile acids:

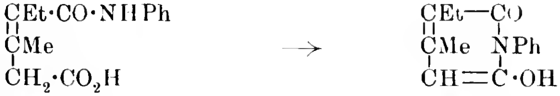
$CO_2H\cdot CMe{:}CMe\cdot CH_2\cdot CO_2H$	$CO_2H\cdot CEt{:}CMe\cdot CH_2\cdot CO_2H$
Labile $\alpha\beta$-acid (m. p. 103°).	Labile β-methyl-α-ethyl acid (m.p. 98°).

As compared with their normal isomerides, these acids possess the characteristic differences of the normal and labile acids of the series. The labile acids are very stable towards alkali, but slowly pass into the normal forms on treatment with hydrochloric acid. Both modifications give the hydroxy-anhydride with equal readiness, and the hydroxy-anhydrides, on hydration with water, give the normal acids. If, however, hydration is effected by strong alkali or by dilute alkali in the presence of casein, the labile acids are produced. Whereas the two modifications of the α-mono-substituted derivatives cannot be distinguished from one another by means of their salts, the two states of the acids described in this paper show important differences in this respect. Thus the normal acids are characterised by giving insoluble and crystalline barium, as well as calcium, salts, whilst the salts of the labile acids with these metals are soluble in water.

The normal acid and the hydroxy-anhydride of αβ-dimethylglutaconic acid, as well as its aniline derivatives, have been already described (Trans., 1911, **99**, 2221). The normal form of β-methyl-α-ethylglutaconic acid has also been described (Trans., 1905, **87**, 1709), but the substance melting at 53° described in that paper as the anhydride is in reality the hydroxy-anhydride, since it behaves on titration as a monobasic acid, yielding salts in accordance with the equation:



The semianilide, melting at 129°, which is formed by the action of aniline on the hydroxy-anhydride, passes into the hydroxy-anil when heated, and the same substance is produced both from the normal and labile acids by the action of aniline at a high temperature:



M. p. 129°. M. p. 95°.

The derivatives of β-methyl α-ethylglutaconic acid are therefore as follows:

Normal acid.	Labile acid.	Hydroxyanhydride.	Anilic acid.	Hydroxyanil.
164°	98°	53°	129°	95°

Experimental.

Normal Ethyl Carbethoxy-αβ-dimethylglutaconate,

$$(CO_2Et)_2\overset{|}{C}\cdot CHMe\cdot\overset{|}{C}Me\cdot CO_2Et$$

The normal ester of the above formula is the sole product formed when an alcoholic solution of the sodium compound,

$$(CO_2Et)_2C{:}CMe\cdot CH{:}C(ONa)\cdot OEt,$$

which is produced in the condensation of ethyl tetrolate and ethyl sodiomalonate (Feist, *Annalen*, 1906, **345**, 82), is heated on the water-bath with excess of methyl iodide. It boils at 177°/20 mm., is not extracted from its ethereal solution by 10 per cent. aqueous potassium hydroxide, and is not coloured by ferric chloride:

0·2103 gave 0·4541 CO_2 and 0·1480 H_2O. C=58·90; H=7·82.

$C_{14}H_{22}O_6$ requires C=58·7; H=7·7 per cent

The ester is converted into normal αβ-dimethylglutaconic acid, melting at 148°, on both acid and alkaline hydrolysis.

Labile Ethyl Carbethoxy-αβ-dimethylglutaconate, $(CO_2Et)_2CH\cdot CMe\colon CMe\cdot CO_2Et$.

When an alcoholic solution of the sodium compound formed by the action of an equivalent amount of alcoholic sodium ethoxide on the normal ester is poured into twice its volume of water (twelve times the weight of alcohol was used to dissolve the sodium), about 65 per cent. regenerated normal ester is extracted by ether, and the remainder is obtained as a mixture of the ketonic and enolic forms of the labile ester on passing carbon dioxide into the yellow aqueous solution.

The equilibrium mixture closely resembles the normal ester in appearance, and boils at 178°/20 mm.; it gives a reddish-purple coloration with ferric chloride:

0·1997 gave 0·4303 CO_2 and 0·1412 H_2O. C = 58·76; H = 7·85.
$C_{14}H_{22}O_6$ requires C = 58·7; H = 7·7 per cent.

When the equilibrium mixture is dissolved in ether, and the solution is shaken with 10 per cent. aqueous potassium hydroxide, about 15 per cent. is extracted as the yellow potassium compound. Carbon dioxide liberates the enolic form from this solution at low temperatures (ice and salt), and the substance formed in this manner is proved to be an almost pure specimen of this individual from the fact that it is completely extracted from its solution in ether by aqueous potassium hydroxide. It gives a deep red ferric coloration with ferric chloride, but slowly reverts to the equilibrium mixture at the ordinary temperature, a change which is rapidly completed on distillation. The ethereal solution from which the enolic individual has been extracted gives at first no coloration with ferric chloride, but rapidly acquires this property, owing to the gradual restoration of equilibrium between the two forms. After remaining for a short time more of the yellow potassium compound can be extracted by aqueous potassium hydroxide. The labile ester, when hydrolysed by acids, is converted into the normal acid, but when hydrolysed by alkali, a mixture of the normal and labile acids is obtained, from which the latter can be isolated by the aid of the barium salt; for this purpose the mixture is converted into the ammonium salt, excess of barium chloride added, and the whole evaporated to dryness. The soluble barium salt, extracted by cold water, gives, when acidified and extracted by ether, an acid which crystallises from benzene, and then melts at 103°. This acid is described fully later in the paper. The insoluble barium salt gave the normal acid, melting at 148°, on treatment in the same way.

Ethyl α-Acetyl-β-methylglutaconate, $CO_2Et\cdot CHAc\cdot CMe\colon CH\cdot CO_2Et$.

This ester can be prepared in the following way. Sodium (11·5 grams) is dissolved in alcohol and added to 100 grams of ethyl *iso*dehydracetate (Duisberg, *Ber.*, 1882, **15**, 1387; *Annalen*, 1882, **213**, 177), mixed with an equal volume of alcohol, and cooled to −5°. The addition must be effected gradually, and the temperature at no stage must exceed 0°. The deep yellow solution is then diluted with an equal volume of water, and carbon dioxide passed into it until the colour is discharged, when the precipitated oil is extracted by ether. It is a moderately viscid liquid, which is coloured deep purple in alcoholic solution by ferric chloride:

0·1856 gave 0·4041 CO_2 and 0·1252 H_2O. C = 59·38; H = 7·49.

$C_{12}H_{18}O_5$ requires C = 59·5; H = 7·4 per cent.

The ester is completely extracted from its solution in ether by aqueous potassium hydroxide, and is therefore probably enolic in structure. When distilled, it passes almost completely into the pyrone derivative from which it was derived.

Labile Ethyl β-Methylglutaconate, $CO_2Et\cdot CH_2\cdot CMe\colon CH\cdot CO_2Et$.

In order to prepare considerable quantities of the substance, 23 grams of sodium were dissolved in 270 grams of alcohol and gradually mixed with 196 grams of ethyl *iso*dehydracetate, the solution being cooled under running water. After being kept for two hours at room temperature, water was added, and the precipitated oil extracted by ether. The ester boils at 167°/68 mm. as a clear, mobile liquid. The yield was 75 per cent. of the theoretical amount:

0·1862 gave 0·4089 CO_2 and 0·1355 H_2O. C = 59·89; H = 8·08.

$C_{10}H_{16}O_4$ requires C = 60·0; H = 8·0 per cent.

The structure of the ester was proved by the formation of the labile acid (m. p. 115—116°) by hydrolysis with alcoholic potassium hydroxide. Hydrolysis with hydrochloric acid yielded a mixture of the normal and labile acids. A quantity of acid material remains dissolved in the alkaline liquid after extracting the above ester, and can be obtained on acidifying and extracting with ether. The greater portion of this is the labile acid ester, described in the next paragraph; but the remainder consists of a substance of higher molecular weight. The whole was etherified by alcohol and sulphuric acid, when the ethereal solution of the product slowly deposited crystals, which, on recrystallisation from alcohol, yielded well-defined needles, melting at 134°:

0·1794 gave 0·4300 CO_2 and 0·0924 H_2O. C=65·36; H=5·72.
$C_{12}H_{12}O_4$ requires C=65·5; H=5·4 per cent.

The substance gives no coloration with ferric chloride, and is insoluble in cold aqueous alkali. When warmed with this reagent, it slowly passes into solution, and acids precipitate another compound, which crystallises from dilute acetic acid in small needle clusters, melting at 141°, eliminating water vapour at a few degrees above this temperature, and then passing into the substance from which it was derived:

0·1578 gave 0·3506 CO_2 and 0·0834 H_2O. C=60·59; H=5·87.
$C_{12}H_{14}O_5$ requires C=60·5; H=5·9 per cent.

0·1271 required 5·35 c.c. NaOH solution (1 c.c.=0·00785 gram NaOH).
$C_{12}H_{14}O_5$ (dibasic) requires 5·44 c.c.

It is evident that these two substances are related to one another as dibasic acid and anhydride, but we have not as yet succeeded in assigning any satisfactory constitution to them.

Labile Ethyl Hydrogen β-Methylglutaconate,
$CO_2H\cdot CH_2\cdot CMe{:}CH\cdot CO_2Et$.

This compound is formed in the experiment described above, but is difficult to obtain pure. It may be prepared by the action of alcoholic sodium ethoxide on the labile ester at the ordinary temperature, and can be isolated by shaking an ethereal solution of the product with aqueous sodium carbonate. It is a moderately viscous liquid, which does not appear to possess any tendency to crystallise:

0·2176 gave 0·4428 CO_2 and 0·1369 H_2O. C=55·50; H=6·99.
$C_8H_{12}O_4$ requires C=55·8; H=7·0 per cent.

The acid ester passes into alcohol and the hydroxy-anhydride on distillation, and is converted into the labile acid on hydrolysis with aqueous potassium hydroxide.

Normal Ethyl β-Methylglutaconate, $CO_2Et\cdot \overset{|}{C}H\cdot CHMe\cdot \overset{|}{C}H\cdot CO_2Et$. —This ester is prepared by the esterification of the normal acid with alcohol and sulphuric acid, and is described in the literature. It yields the pure normal acid on hydrolysis with both acids and alkalis unless a large excess of the latter is used.

Normal Ethyl Hydrogen β-Methylglutaconate,
$CO_2Et\cdot \overset{|}{C}H\cdot CHMe\cdot \overset{|}{C}H\cdot CO_2H$.

This substance occurs as a by-product in the etherification of the normal acid, and can be extracted by aqueous sodium carbonate.

It crystallises from light petroleum (b. p. 70—80°) containing a little benzene, in long, slender needles, which melt at 73°:

0·1960 gave 0·4005 CO_2 and 0·1256 H_2O. C=55·72; H=7·12.

$C_8H_{12}O_4$ requires C=55·8; H=7·0 per cent.

The acid ester passes into alcohol and the hydroxy-anhydride when slowly distilled, and yields the normal acid on hydrolysis with alkali under the same conditions as those which transform the labile acid-ester into the labile acid. It is readily soluble in all the usual organic solvents excepting light petroleum.

Labile Ethyl αβ-Dimethylglutaconate,
$CO_2Et\cdot CMe\colon CMe\cdot CH_2\cdot CO_2Et$.

In order to prepare this substance, 4·6 grams of sodium were dissolved in 55 grams of alcohol and gradually mixed with 40 grams of ethyl *iso*dehydracetate diluted with an equal volume of alcohol, the mixture being kept at 0° throughout the process. Methyl iodide (31 grams) was then added, and the solution kept at about 5° for two hours, when the reaction was brought to completion by gently warming on the water-bath. The ester, isolated in the usual manner, boiled at 142°/20 mm. as a colourless, mobile oil:

0·1884 gave 0·4258 CO_2 and 0·1455 H_2O. C=61·63; H=8·58.

$C_{11}H_{18}O_4$ requires C=61·7; H=8·4 per cent.

The ester yields the normal acid (m. p. 148°) on hydrolysis with hydrochloric acid, and is converted into the labile acid (see below) on hydrolysis with alkali. The ethyl acetate formed in the reaction was recognised by its odour, but was not isolated.

Normal Ethyl αβ-Dimethylglutaconate,

$CO_2Et\cdot\overset{|}{C}Me\cdot CHMe\cdot\overset{|}{C}H\cdot CO_2Et$.

This substance is best prepared by the etherification of the normal acid with alcohol and sulphuric acid in the usual manner. It boils at 141°/21 mm. as a mobile liquid, closely resembling the labile ester in appearance:

0·2439 gave 0·5495 CO_2 and 0·1864 H_2O. C=61·45; H=8·49.

$C_{11}H_{18}O_4$ requires C=61·7; H=8·4 per cent.

The ester gives the normal acid on both acid and alkaline hydrolysis.

Labile αβ-Dimethylglutaconic Acid, $CO_2H\cdot CMe\colon CMe\cdot CH_2\cdot CO_2H$.

This acid, formed from the labile ester on hydrolysis with twice the theoretical amount of alcoholic potassium hydroxide, is obtained in a pure condition by recrystallisation from benzene, from which solvent it separates in small needles melting at 103°:

0·1836 gave 0·3578 CO_2 and 0·1052 H_2O. C=53·15; H=6·37.
$C_7H_{10}O_4$ requires C=53·2; H=6·3 per cent.

The acid is very unstable towards mineral acids, and in the above preparation care must be taken to liberate the acid from the potassium salt with the theoretical amount of hydrochloric acid; otherwise in the presence of excess of acid some of the labile modification is converted into the normal acid; in fact, the labile acid is much less stable in the presence of hydrochloric acid than the corresponding labile modification of β-methylglutaconic acid. The action of boiling aqueous potassium hydroxide which was found to convert the normal form of β-methylglutaconic acid completely into the labile modification (Feist) is only partly effective in the case of the higher homologue. The mixed acids produced in this manner can be readily separated, owing to the fact that the normal acid gives an insoluble, crystalline barium salt when the ammonium salt is treated with barium chloride and the solution is boiled:

0·3772 gave 0·2990 $BaSO_4$. Ba=46·61.
$C_7H_8O_4Ba$ requires Ba=46·7 per cent.,

whereas the salt of the labile acid remains in solution. The calcium salts of the two forms show the same difference in behaviour. The labile acid is more soluble in water than the normal acid.

The *silver* salt is a white, micro-crystalline powder:

0·3125 gave 0·1812 Ag. Ag=57·98.
$C_7H_8O_4Ag_2$ requires Ag=58·06.

The labile acid is very stable towards boiling aqueous solutions of alkaline hydroxides.

Labile Ethyl β-Methyl-α-ethylglutaconate,
$CO_2Et{\cdot}CEt{:}CMe{\cdot}CH_2{\cdot}CO_2Et$.

This compound is prepared in the same manner as the dimethyl ester. It is a mobile liquid, which boils at 144°/15 mm.:

0·2369 gave 0·5472 CO_2 and 0·1898 H_2O. C=62·98; H=8·90.
$C_{12}H_{20}O_4$ requires C=63·2; H=8·8 per cent.

The ester yields the normal form of β-methyl-α-ethylglutaconic acid (Trans., 1905, **87**, 1709) when hydrolysed by acids, but is converted into the labile acid by alkalis.

Normal Ethyl β-Methyl-α-ethylglutaconate,

$CO_2Et{\cdot}\overset{|}{C}Et{\cdot}CHMe.\overset{|}{C}H_2{\cdot}CO_2Et.$

The ester is formed from the normal acid on etherification by alcohol and sulphuric acid. It boils at 143°/15 mm.:

0·2276 gave 0·5263 CO_2 and 0·1822 H_2O. C = 63·05; H = 8·89.

$C_{12}H_{20}O_4$ requires C = 63·2; H = 8·8 per cent.

It is converted into the normal acid on both acid and alkaline hydrolysis.

Labile β-Methyl-α-ethylglutaconic Acid,

$CO_2H{\cdot}CEt{:}CMe{\cdot}CH_2{\cdot}CO_2H.$

This acid is formed by the hydrolysis of the labile ester with twice the theoretical amount of alcoholic potassium hydroxide, care being taken to add only the requisite quantity of hydrochloric acid to liberate the acid from its salt. It separates from either water or benzene in needle clusters, which melt at 98°:

0·1753 gave 0·3600 CO_2 and 0·1130 H_2O. C = 56·02; H = 7·16.

$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

The acid is more stable towards hydrochloric acid than the dimethyl acid, but is slowly converted into the normal modification when warmed with this reagent. It differs from the normal acid in being readily soluble in dry ether and in hot benzene; it is, moreover, more soluble in water than the higher melting acid. The barium and calcium salts of the two forms differ in the same way as the salts of the corresponding dimethyl acids.

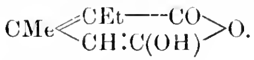
The *silver* salt is a white, crystalline powder:

0·3210 gave 0·1791 Ag. Ag = 55·79.

$C_8H_{10}O_4Ag_2$ requires Ag = 55·95 per cent.

The normal acid is converted into a mixture of the two modifications on prolonged boiling with strong aqueous alkali, the mixture being easily separated by means of the barium salts.

The Hydroxy-anhydride of β-Methyl-α-ethylglutaconic Acid
(*6-Hydroxy-4-methyl-3-ethyl-α-pyrone*),



$$CMe{<}\begin{matrix}CEt\text{———}CO\\ CH{:}C(OH)\end{matrix}{>}O.$$

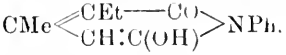
This substance is obtained with equal readiness both from the normal and labile acids through the agency of acetyl chloride. It was described as the normal anhydride in a previous paper (Trans., 1905, **87**, 1709), and is best prepared by the method there given. It behaves on titration as a monobasic acid:

0·3125 required 10·2 c.c. NaOH-solution (1 c.c. = 0·0078 gram NaOH).

$C_8H_{10}O_3$ (monobasic) requires 10·28 c.c.

The hydroxy-anhydride is converted into the normal acid by hydration with water, and into the labile acid on treatment with dilute alkali in the presence of casein.

The Hydroxy-anil of β-Methyl-α-ethylglutaconic Acid (3-*Hydroxy*-2-*phenyl*-5-*methyl*-6-*ethyl*-1 : 2-*dihydropyridone*),



$$\mathrm{CMe}\!<\!\begin{matrix}\mathrm{CEt{-\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\!>\!\mathrm{NPh}.$$

This substance can be obtained either by heating the semianilide (Trans., 1905, **87**, 1709) at 150°, or by the direct action of aniline on the acid. In the latter case, 1·3 grams of acid were mixed with 0·7 gram of aniline, and heated at 150° for fifteen minutes. The product was rubbed with a little pure ether, and recrystallised from this solvent. It formed long needles melting at 95°:

0·2109 gave 0·5673 CO_2 and 0·1281 H_2O. C = 73·35; H = 6·74.

$C_{14}H_{15}O_2N$ requires C = 73·4; H = 6·6 per cent.

The anil is readily soluble in benzene, and dissolves in alkalis, behaving on titration as a monobasic acid:

0·2731 required 6·1 c.c. NaOH-solution (1 c.c. = 0·0078 gram NaOH).

$C_{14}H_{15}O_2N$ (monobasic) requires 6·12 c.c.

The colour of the indicator does not return on keeping, and the ring is not broken when the neutral solution is boiled.

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CLXIX.—*Studies on Certain Aliphatic Hydroxy-acids.*

By HENRY JOHN HORSTMAN FENTON and WILLIAM ARTHUR REGINALD WILKS.

DURING a course of investigations on the oxidation of organic compounds in presence of iron as catalyst, a considerable number of new substances have been brought to light, and several relationships of interest have been observed, especially amongst the hydroxy-acids of the three-carbon and four-carbon series (Trans., 1904, **65**, 899; 1895, **67**, 48, 744; 1896, **69**, 546; 1897, **71**, 375; 1898, **73**, 71; 1900, **77**, 77; 1902, **81**, 426; 1905, **87**, 804; etc.).

These investigations are being continued by the present authors, and an account is here given of some of the results which have recently been obtained.

Oxalacetic Acid and its Relationship to Dihydroxymaleic Acid.

It has been shown by Fenton and Jones (*loc. cit.*, 1900, **77**, 77) that, by the oxidation of malic acid by hydrogen dioxide in presence of ferrous iron, oxalacetic acid is obtained. The acid is isolated from the reaction mixture by addition of concentrated sulphuric acid and extraction with ether; when prepared in this manner, the product melts at 180—184°. Wohl and Oesterlin (*Ber.*, 1901, **34**, 1139) afterwards showed that by action of pyridine on diacetyltartaric anhydride and decomposition of the resulting compound with dilute acids, an acid of the composition and properties of oxalacetic acid is obtained, which, however, melts at 152°. Later it was found that this product when dissolved in sulphuric acid (30 per cent.) and extracted with ether is converted into the modification melting at 184°. From measurements of molecular refraction, and from the behaviour of the acids towards ferric chloride, potassium permanganate, etc., Wohl concludes that both acids are enolic, the difference between them being ascribed to geometrical isomerism. If this is admitted, it is evident from the melting points, mode of transformation, and anhydride formation, that the acids melting at 184° and 152° are hydroxyfumaric and hydroxymaleic acids respectively.

The constitution of dihydroxymaleic acid was inferred (Trans., 1905, **87**, 804) from the readiness with which anhydride formation occurs and from the fact that an acid, apparently isomeric, is produced from it by action of fuming hydrobromic acid. This configuration was not insisted on, however, since the mode of formation from *d*-tartaric acid, and the production of racemic acid by action of hydriodic acid, would be more easily explained if the acid is regarded as dihydroxyfumaric acid.*

Some light is thrown on these problems by the recent observations of the present authors, since they find that the modification of "oxalacetic acid" of higher melting point can be directly transformed into "dihydroxymaleic acid."

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* It has been suggested that the initial form of the acid, obtained in aqueous solution, may be trihydroxysuccinic acid or the keto-acid, $CO_2H\cdot CH(OH)\cdot CO\cdot CO_2H$ (compare Nef, *Annalen*, 1910, **376**, 116), and that this form is changed by the concentrated sulphuric acid used in the preparation. Recent experiments show, however, that the usual form, crystallising in diamond-shaped plates, is obtained, without the use of sulphuric acid, by evaporation of the original solution in a vacuum.

When oxalacetic acid (m. p. 180—184°) is dissolved in a cold solution of sodium hydroxide in slight excess, and bromine is gradually added in one molecular proportion, the solution being maintained alkaline, the resulting solution gives an intense violet colour with ferric chloride; addition of dilute sulphuric acid changes this to a transient green. If the solution is just acidified with acetic acid and barium acetate is added, a bulky, white precipitate is obtained, which, when decomposed with dilute sulphuric acid, yields again the same colour reactions with ferric salts.

This barium salt when dried in a vacuum desiccator and afterwards at 100° gave the following result on analysis:

0·2906 gave 0·2399 $BaSO_4$. Ba = 48·53.

$C_4H_2O_6Ba$ (barium dihydroxymaleate) requires Ba = 48·40 per cent.

If the original solution, after addition of bromine, is acidified with sulphuric acid and extracted with ether, a residue is obtained on evaporation of the ethereal solution which, when dissolved in warm water, gives, on cooling, the characteristic diamond-shaped plates of dihydroxymaleic acid. A similar result is obtained by decomposing the dried barium salt with dilute sulphuric acid. From this result it would appear that, if "the spatial relations of the original molecule persist in the new product," the geometrical configuration of the "oxalacetic" acid of higher melting point must be the same as that of "dihydroxymaleic acid." Presumably, therefore, the result must be regarded as evidence in favour of ascribing the fumaroid configuration to the latter acid. The result, however, might be accounted for in other ways; thus, Wohl considers that the normal salts of oxalacetic acid have the keto-form, and that when these are decomposed with dilute acids the less stable maleinoid form first arises, in accordance with Ostwald's rule. In the present case, therefore, the keto-form of oxalacetic acid may give the corresponding form of "dihydroxymaleic acid," and this on acidification may undergo a similar transformation to the maleinoid form.

Bromo-oxalacetic Anhydride or *Bromohydroxymaleic Anhydride.*

The oxidation of oxalacetic acid to dihydroxymaleic acid referred to in the last section may be effected in two stages, the free acid being brominated in water, ether, alcohol, etc., as solvent, and the product then acted on by alkali hydroxides. The initial stage appears to be of considerable interest, and the product has, after some difficulty, been isolated in the form of its anhydride.

When oxalacetic acid is dissolved in ether and bromine is slowly added, the colour of the bromine is instantly discharged until nearly the calculated quantity (1 mol.) has been added. If the resulting solution is now rapidly distilled, under diminished pressure, to remove the ether and hydrogen bromide, a syrup remains which sometimes partly sets to a buttery, crystalline mass. This product again gives the intense violet colour when treated with alkali hydroxide and ferric chloride. The product is, however, remarkably unstable; if it is kept overnight in a vacuum desiccator, a considerable quantity of hydrogen bromide is liberated, and crystals of oxalacetic acid (m. p. 180—184°) separate. About half the original acid can be actually recovered in this way. The mother liquor from these crystals now no longer gives the violet colour with ferric salts and alkali; but sodium hydroxide or carbonate produces a white precipitate and phenylhydrazine an orange precipitate, which, after crystallisation from alcohol, melts at 203°.

A possible explanation of this remarkable change is that the initial product is bromohydroxyfumaric acid; that the group $\cdot C(OH){:}CBr\cdot$ is unstable, and that the two molecules of the acid resolve themselves into oxalacetic and dihydroxytartaric acids, hydrogen bromide being evolved:

$$2CO_2H\cdot C(OH){:}CBr\cdot CO_2H + H_2O = \\ CO_2H\cdot C(OH){:}CH\cdot CO_2H + CO_2H\cdot CO\cdot CO\cdot CO_2H + 2HBr.$$

Since, however, water would be necessary to complete this change, it may be assumed that the anhydride of dihydroxytartaric acid is produced instead of the acid.

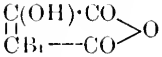
Regarding the matter from this point of view, it appeared probable that acetylation of the hydroxy-group in bromohydroxyfumaric acid might yield a product of greater stability, and it was found that if the product obtained as described above (by bromination and distilling off the ether) is immediately heated with acetyl chloride or acetic anhydride, its colour-giving property remains much more permanent. Proceeding in this way, however, it was found impossible to obtain any crystalline compound, so that the experiment was modified as follows:

The oxalacetic acid was dissolved in hot glacial acetic acid, the solution cooled, and the calculated quantity of bromine run in. Excess of acetyl chloride was then added, and the mixture kept boiling in a reflux apparatus for about fifteen minutes. The solvent was then distilled off under greatly diminished pressure, and the residual syrup left in a vacuum desiccator over sulphuric acid and potassium hydroxide. After remaining for a day or two, large, semi-transparent prisms separated; these were drained, pressed, and recrystallised from dry ether. The crystals so obtained melt at 114—116°. They dissolve readily in water, and the solution gives at once the characteristic intense violet colour with ferric chloride in presence of alkali hydroxide. With ferric chloride alone an intense red colour is obtained.

Analysis shows that this product is not an acetyl derivative, as was at first expected, but an anhydride of bromo-oxalacetic acid:

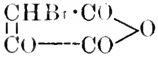
0·2019 gave 0·1833 CO_2 and 0·0144 H_2O. C=24·8; H=0·79.
0·2796 „ 0·2704 AgBr. Br=41·2.
C_4HO_4Br requires C=24·8; H=0·52; Br=41·4 per cent.

The product is therefore either



$$\begin{array}{l}C(OH)\cdot CO \\ \| \\ CBr—CO\end{array}\!\!>O$$

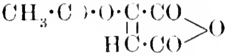
or



$$\begin{array}{l}CHBr\cdot CO \\ | \\ CO—CO\end{array}\!\!>O$$

When oxalacetic acid itself is treated under similar conditions, without bromination, with acetic acid and acetyl chloride, a crystalline product results, which, when recrystallised from ether, melts at 88—89°. (Found, C=45·5; H=2·7. $C_6H_4O_5$ requires C=46·1; H=2·5 per cent.)

This compound is evidently identical with the acetoxymaleic anhydride:



$$\begin{array}{r}CH_3\cdot CO\cdot O\cdot C\cdot CO \\ \| \quad\;\; \\ HC\cdot CO\end{array}\!\!>O$$

(m. p. 89—91°), which Michael obtained by the action of acetic anhydride on acetylenedicarboxylic acid (*Ber.*, 1895, **28**, 2511).

From these observations it would appear, regarding oxalacetic acid as the hydroxy-form, that the initial bromination prevents acetylation. This circumstance might be ascribed either to the steric hindrance of the bromine atom or to a tautomeric change to the keto-form during one of the operations involved.

The bromine in this compound is extremely reactive, and a further study of its reactions will probably be of much interest.

Isomeric Esters of Dihydroxymaleic Acid.

The ethyl and methyl esters of dihydroxymaleic acid are readily obtained by the usual method. The alcoholic solution of the acid is saturated, or nearly saturated, with hydrogen chloride, and the mixture allowed to remain. The methyl ester separates to a large extent after a few hours. In the case of the ethyl ester the liquid is distilled to small volume under diminished pressure, when the residual liquid sets, on cooling, to a crystalline mass.

It was previously shown that each of these esters exists in two modifications having distinct crystalline forms, but the differences were not further investigated. The two forms of the ethyl ester have now been more closely studied, with the following results: The crystalline mass obtained in the preparation, described above, is well drained, pressed, and allowed to dry in the air. It is then digested with ether. One portion dissolves immediately, and crystallises from this solution in long, silky needles (form A). The portion remaining is only very sparingly soluble in ether; it is washed repeatedly with ether, and is then found to consist of short, rod-like prisms (form B). In other organic solvents, also, the (A) form has a much greater solubility. Both forms give the same result on analysis:

(A) 0·1605 gave 0·2752 CO_2 and 0·0822 H_2O. $C=46·7$; $H=5·69$.
(B) 0·1251 ,, 0·2113 CO_2 ,, 0·0660 H_2O. $C=47·0$; $H=5·4$.
$C_8H_{12}O_6$ requires $C=47·05$; $H=5·88$ per cent.
(A) melts at 68°, (B) at 126—128°.

Further points of difference are the following:

(1) Alcoholic ferric chloride gives a dark but transient green colour with an alcoholic solution of (A); no colour with (B).

(2) Alkali hydroxides give at once a lemon-yellow colour with (A) and no colour with (B).

(3) Phenylhydrazine reacts slowly with both forms when they are heated with the reagent in alcoholic solution, but with (A) the change is much more rapid. The product eventually obtained is, as previously shown, the pyrazolone derivative which Anschütz and Parlato prepared from ethyl dihydroxytartrate (dioxysuccinate). It crystallises in orange needles melting at 154° (Trans., 1905, **87**, 810).

(4) When the (A) form is mixed with acetyl chloride it dissolves immediately, and after boiling in a reflux apparatus for a short time and removal of the excess of solvent, yields a crystalline mass. This product (ethyl diacetoxymaleate,

$$CO_2Et\cdot C(OAc)\colon C(OAc)\cdot CO_2Et)$$

dissolves unchanged in boiling water, and separates on cooling in fine needles, which melt at 68°:

0·1502 gave 0·2731 CO_2 and 0·0737 H_2O. $C=49·6$; $H=5·4$.
$C_{12}H_{16}O_8$ requires $C=50·0$; $H=5·5$ per cent.

The form (B) when boiled for an hour or more with considerable excess of acetyl chloride is scarcely affected. The greater part remains insoluble, and the small quantity which passes into solution leaves, on evaporation, only a syrup, which does not crystallise even on keeping in a desiccator.

The experiment was then repeated with acetic anhydride in place of acetyl chloride. In this the (B) ester dissolves at once on warming. After heating on a water-bath for half an hour, and distilling off the solvent under diminished pressure, the residue set to a mass of long needles. This product was found to have all the properties of the (A) ester, and gave the same result on analysis. It was subsequently found that the (A) ester is not altered by treatment with acetic anhydride in similar circumstances.

The effect of heating the (B) ester with acetic anhydride is therefore merely its conversion into the (A) form.

(5) In a previous communication (*loc. cit.*) it has been stated that the ethyl ester of dihydroxymaleic acid undergoes a remarkable change when kept in a desiccator over sulphuric acid or phosphoric oxide in presence of air. In these circumstances it becomes partly or entirely converted into a yellow liquid after about twelve hours; this change is attended at first with a slight increase in weight, after which the weight regularly diminishes, the loss continuing for some weeks. When kept in the atmosphere at the ordinary temperature the ester is quite stable, and remains unaltered for months. These experiments were made with the initial product obtained in the preparation of the ester, or with the same recrystallised from ether, and the fact of the existence of two forms was not then recognised. It is now found that it is only the (A) form that undergoes this change. The (B) form remains quite unaltered when kept in the desiccator, in presence of air, at any rate, for some weeks. This difference in the behaviour of the two forms is most striking, and it may perhaps afford evidence with regard to the character of the isomerism.

The nature of the change which takes place when the (A) ester undergoes liquefaction in this way was at first not easy to understand. It is now found, however, that the resulting liquid product when dissolved in alcohol reacts at once with phenylhydrazine, and yields the pyrazolone derivative melting at 154°, which has been referred to above. Presumably, therefore, the change consists in the oxidation and dehydration of ethyl dihydroxymaleate to ethyl dioxosuccinate:

$$CO_2Et{\cdot}C(OH){:}C(OH){\cdot}CO_2Et + O = CO_2Et{\cdot}CO{\cdot}CO{\cdot}CO_2Et + H_2O,$$

a supposition which would also account for the yellow colour of the product. Even if this simple explanation is the true one, it is somewhat remarkable that the dehydration is essential.

(6) A dilute aqueous solution of potassium permanganate is instantly decolorised when added to a solution of (A) in acetone, whereas a solution of (B) in the same solvent is only slowly affected at first; the colour in the latter case persists for a minute or so.

In addition to the behaviour of the two esters towards the reagents mentioned, there are many other points of difference which are being further studied. The isomerism in this case appears to be of particular interest because of the very sharp differences in properties and the persistence of the two forms.

In attempting to account for these remarkable differences, the very commonly occurring problem is encountered of deciding whether the phenomenon is one of keto-enolic isomerism or of geometrical isomerism. The same problem presents itself in oxalacetic acid, and appears, as above mentioned, to have been successfully solved by Wohl, although differences of opinion may still exist with regard to his conclusions.

In the present case the authors are inclined to attribute the difference to keto-enolic isomerism, which would easily account for most of the facts, such as the behaviour towards ferric chloride, acetyl chloride, potassium permanganate, and phenylhydrazine. The alternative hypothesis is, however, by no means excluded, and would afford perhaps a more simple explanation of the peculiar behaviour of the (A) ester when dehydrated in presence of oxygen.

Aldehydoglyceric Acid.

It was found by Fenton and Jones (Trans., 1900, **77**, 73) that when glyceric acid is oxidised by hydrogen dioxide in presence of ferrous iron, a product is obtained which gives an intense bluish-violet colour with ferric salts in presence of alkali, and which when acted on by phenylhydrazine yields the osazone,

$$CH(\vdots N_2HPh)\cdot C(\vdots N_2HPh)\cdot CO_2H,$$

which Nastvogel first obtained from dibromopyruvic acid. This product is of much interest, owing to its relationship with the acid which Will obtained by action of alkalis on collodion wool. The present authors have therefore made a further study of this product, and have succeeded in obtaining it in the crystalline state, although only in small quantities, and not entirely free from admixed solvents.

After oxidation of glyceric acid in the manner previously described, the mixture is treated with calcium carbonate in order to remove small quantities of oxalic acid (which are usually formed in the reaction unless special care is taken), and lead acetate is then added in excess. A bulky, yellow precipitate is thus produced, which, when well washed and decomposed by hydrogen sulphide (avoiding excess), gives a solution having the properties referred to above. The conditions of dilution, etc., chosen are such as to preclude the possibility of the separation of lead glycerate, should any of this acid remain unoxidised.

For analysis, this lead salt was well washed with water, alcohol, and ether, and then dried at 100°:

0·4185 gave 0·3873 $PbSO_4$. $Pb = 63·4$.

$(C_3H_3O_4)_2Pb,PbO,H_2O$ requires $Pb = 63·3$ per cent.

The calcium salt was obtained by neutralising the purified solution of the acid with calcium carbonate and precipitating by alcohol. This, when dried in a desiccator, gave the following numbers:

0·2374 gave 0·1124 $CaSO_4$. Ca = 13·9.

$(C_3H_3O_4)_2Ca,2H_2O$ requires Ca = 14·2 per cent.

With the same salt dried at 100°:

0·1928 gave 0·1105 $CaSO_4$. Ca = 15·3.

$(C_3H_3O_4)_2Ca,H_2O$ requires Ca = 15·1 per cent.

If the lead salt, thoroughly washed with water, alcohol, and ether, is covered with dry acetone and carefully decomposed by hydrogen sulphide, and the resulting solution is kept in a vacuum desiccator, a syrup is left. This, when dissolved in ether and mixed with light petroleum until a turbidity is produced, yields after a day or two white crystals, which firmly adhere to the sides of the flask. These crystals are extremely hygroscopic, and there is considerable difficulty in separating them completely from the mother liquor. When dissolved in water they give the characteristic colour with ferric chloride and alkali. (In this case the colour is somewhat slowly developed, a property which is also observed when a solution of the acid prepared from the lead salt in aqueous solution is kept.)

For analysis, the crystals were dissolved off the sides of the flask with ether, and the solution kept in a vacuum desiccator. The result evidently indicates that the product retains traces of the solvent:

0·2155 gave 0·2785 CO_2 and 0·0785 H_2O. C = 35·2; H = 4·0.

$C_3H_4O_4$ requires C = 34·6; H = 3·8 per cent.

From the properties mentioned and from the analyses, it follows that the acid under consideration is either hydroxypyruvic acid, $CH_2(OH)\cdot CO\cdot CO_2H$, tartronic semialdehyde, $CHO\cdot CH(OH)\cdot CO_2H$, or the tautomeric dihydroxyacrylic acid, $CH(OH)\colon C(OH)\cdot CO_2H$.

Will (*Ber.*, 1891, **24**, 400) regarded the acid obtained from collodion wool as hydroxypyruvic acid, because of its stability towards bromine and towards alkalis. He stated, however, that the acid is feebly lævorotatory. Since no asymmetric carbon atom is present in hydroxypyruvic acid, it was obvious that further investigation was necessary. Aberson afterwards (*Zeitsch. physikal. Chem.*, 1899, **31**, 17) drew the conclusion that the optical activity is due to impurity, and found that the acid when acted on by hydrocyanic acid, and the product hydrolysed with barium hydroxide, gave rise to glyceric acid. Hence it would appear that the acid is hydroxypyruvic acid, the glyceric acid being the result of decomposition of the "*iso*tartaric" acid,

$$CH_2(OH)\cdot C(OH)(CO_2H)_2,$$

first produced.

An entirely different conclusion was subsequently arrived at by Neuberg and Silbermann (*Zeitsch. physiol. Chem.*, 1905, **44**, 134). They state that the acid is lævorotatory, and that by action of potassium cyanide they obtain *l*-tartaric acid. By reduction of the original acid with sodium amalgam, *l*-glyceric acid was obtained. For these reasons they assign the formula $CHO\cdot CH(OH)\cdot CO_2H$ to the acid, and name it "aldehydoglyceric" acid.

In view of these contradictory statements, it appeared that additional evidence was desirable, and it seemed probable that the properties of the acid obtained from glyceric acid by oxidation might throw light on the question. The latter acid is sharply distinguished from Will's acid by the colour reaction with ferric chloride; also by the fact that it is destroyed by heating on a water-bath, a process employed during the preparation of Will's acid.

The acid was obtained in aqueous solution by oxidation of glyceric acid, precipitation as lead salt, and decomposition with hydrogen sulphide. A solution of potassium cyanide, somewhat in excess, was added, and the mixture allowed to remain for about ten days in a closed vessel. The dark-coloured liquid so obtained was treated with a quantity of *N*-sulphuric acid equivalent to the potassium cyanide employed, and heated for about half-an-hour. Barium hydroxide was then added in calculated quantity, the filtered solution concentrated, and precipitated with lead acetate. The precipitate obtained in this way was washed and decomposed under water with hydrogen sulphide, avoiding excess. Ammonia in slight excess was added to the solution, and then calcium chloride; the resulting calcium glycerate, $(C_3H_5O_4)_2Ca,2H_2O$, was purified by dissolving in hot water and precipitating with alcohol. (Found, Ca = 14·2. Calc., Ca = 14·0 per cent.)

This result, so far as it goes, points to the hydroxypyruvic acid formula for the acid obtained by oxidation of glyceric acid, and consequently would appear to add confirmation to the results of Neuberg and Silbermann. The question of tautomeric change has, however, to be considered, and from the character of the ferric chloride reaction (which closely resembles that of dihydroxymaleic acid) it seems most probable that the product is originally present, principally, at any rate, as dihydroxyacrylic acid.

Action of Semicarbazide.—When this product of oxidation of glyceric acid is mixed with a solution of semicarbazide hydrochloride, white crystals appear after some time, which, after recrystallisation from acetic acid, melt at 221°, and appear to consist of the semicarbazide salt of the semicarbazone,

$$CH_2(OH)\cdot C{:}(N\cdot NH\cdot CO\cdot NH_2)\cdot CO_2H,NH_2\cdot NH\cdot CO\cdot NH_2:$$

0·1423 gave 0·1310 CO_2 and 0·060 H_2O. C = 25·1; H = 4·68.
0·1201 „ 36·8 c.c. N_2 at 15° and 740 mm. N = 35·5.
$C_5H_{12}O_5N_6$ requires C = 25·4; H = 5·07; N = 35·6 per cent.

It is interesting to observe that a compound identical in every respect with the foregoing is obtained when dihydroxymaleic acid in aqueous solution is mixed with semicarbazide hydrochloride and allowed to remain. This result affords further evidence in support of the view previously expressed (Trans., 1905, **87**, 806) that the loss of carbon dioxide from dihydroxymaleic acid probably takes place in two stages, the products being dihydroxyacrylic acid (or its tautomeric form) and glycollaldehyde respectively.

Condensations with Carbamide.

It was shown by the present authors (Trans., 1909, **95**, 1329) that dihydroxymaleic acid when heated alone with carbamide gives rise to a crystalline compound having the molecular formula $C_3H_4ON_2$, which, in most of its properties, closely resembles Marckwald's iminazolone (glyoxalone). Since, however, there appeared to be certain important points of difference, the term "*iso*iminazolone" was provisionally adopted.

In addition to this compound, the condensation of carbamide with dihydroxymaleic acid gives rise to a considerable number of other products, some of which appear to be of particular interest.

When the acid (1 mol.) is heated with carbamide (2 mols.) and excess of phosphorus pentachloride, a product is obtained which, after treatment with excess of barium hydroxide, gives a very intense murexide reaction when evaporated with hydrochloric acid containing nitric acid. This product can be partly separated by cupric acetate, a yellowish-brown precipitate being formed, from which it can be recovered by hydrogen sulphide. In these and other of its properties, the product appears to show a remarkable resemblance to xanthine, the formation of which could be accounted for in accordance with the simple relation:

$$C_4H_4O_6 + 2CH_4ON_2 = C_5H_4O_2N_4 + 4H_2O + CO_2,$$

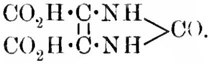
although isomeric rearrangement would, of course, have to be assumed.

So far, it has not been found possible to obtain this product in a sufficiently pure state for analysis, and many other methods have been attempted for effecting the condensation without the use of phosphorus haloids. The ethyl esters, or the diacetyl-anhydride, when simply melted with carbamide, yield products which give the murexide reaction, but the quantity is very small.

When the ethyl ester (1 mol.) and carbamide (2 mols.) are melted together, dry hydrogen chloride passed into the mixture, and the temperature kept at about 140° for an hour, a yellow solid is obtained, which when boiled with excess of sodium hydroxide partly dissolves. If the less soluble portion is dissolved in hot hydrochloric acid and allowed to cool slowly, a mass of colourless, silky needles separates. For analysis they were dried in a vacuum desiccator:

0·1681 gave 0·2105 CO_2 and 0·0381 H_2O. $C=34·15$; $H=2·51$.
0·1631 ,, 22 c.c. N_2 at 15° and 754 mm. $N=16·0$.
$C_5H_4O_5N_2$ requires $C=34·8$; $H=2·32$; $N=16·27$ per cent.

From these numbers and from the mode of formation it would appear that the substance is *glyoxalone*-4:5-*dicarboxylic acid*,



$$\left.\begin{array}{l} CO_2H\cdot C\cdot NH \\ \qquad \| \\ CO_2H\cdot C\cdot NH \end{array}\right> CO.$$

This product does not give the murexide reaction. The part more soluble in sodium hydroxide yields another crystalline substance, which has not yet been examined; it gives the murexide reaction, but not very strongly.

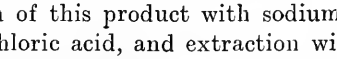
The experiment was then varied by dissolving dihydroxymaleic acid in alcohol, adding excess of carbamide, and saturating the mixture with hydrogen chloride. On allowing to remain for some time and evaporation of the solvent, a crystalline product was obtained, which melted at 258—259°, and consisted of *ethyl glyoxalone*-4:5-*dicarboxylate*:

0·2070 gave 26·9 c.c. N_2 at 16° and 754 mm. $N=12·1$.
$C_9H_{12}O_5N_2$ requires $N=12·3$ per cent.

The behaviour of dihydroxytartaric acid under similar conditions is of interest in comparison with this result; thus, a solution of free dihydroxytartaric acid with excess of carbamide in alcohol, when saturated with hydrogen chloride, yields a crystalline product melting at 245°.

Found: $C=42·1$; $H=4·85$; $N=19·6$.
$C_{10}H_{14}O_6N_4$ requires $C=41·9$; $H=4·89$; $N=19·6$ per cent.

This product is evidently identical with the compound which Anschütz and Geldermann obtained from carbamide and ethyl dioxosuccinate (*Annalen*, 1891, **261**, 129), and which, presumably, may be regarded as ethyl glycolurildicarboxylate,



$$CO\left<\begin{array}{l} NH\cdot C(CO_2Et)\cdot NH \\ NH\cdot C(CO_2Et)\cdot NH \end{array}\right>CO.$$

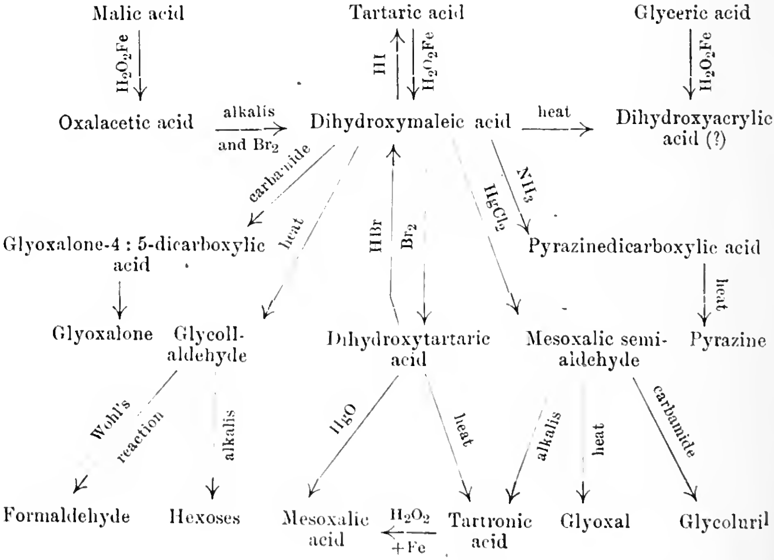
By saponification of this product with sodium hydroxide, acidification with hydrochloric acid, and extraction with alcohol, the free acid was obtained as a crystalline product melting at 195—200°. (Found, $N=24·1$. $C_6H_6O_6N_4$ requires $N=24·3$ per cent.)

It has previously been shown (*loc. cit.*) that dihydroxymaleic acid when oxidised by mercuric chloride and acted on by carbamide yields glycoluril.

It may be mentioned here that dihydroxytartaric acid when mixed with carbamide in alcoholic solution yields a well crystallised urea salt, which when heated to 100° for a short time decomposes, giving carbamide and a sparingly soluble, crystalline product, which melts at 218°, and is easily identified as hydantoin. (Found, N = 28·15. $C_3H_4O_2N_2$ requires N = 28·0 per cent.) The change appears to be practically quantitative, and may be represented as:

$$C_4H_6O_8\cdot 2CO(NH_2)_2 = C_3H_4O_2N_2 + CO(NH_2)_2 + 3H_2O + 2CO_2.$$

The relationships of some of the principal compounds described in the foregoing and other communications, and the transformations which have, so far, been actually accomplished, will be seen at a glance from the subjoined table:

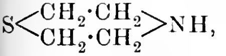


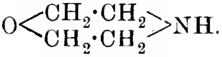
The cost of some of the materials used in this investigation was defrayed by a grant from the Government Grant Committee of the Royal Society.

University Chemical Laboratory,
Cambridge.

CLXX.—4-*Alkyl*-1 : 4-*thiazans*.

By Hans Thacher Clarke (1851 Exhibition Scholar).

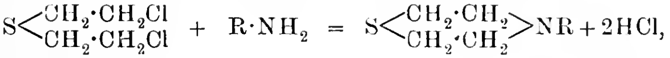
In the course of a study of residual affinity in heterocyclic compounds, the results of which it is hoped shortly to communicate to the Society, the author has had occasion to prepare and examine some alkyl derivatives of the heterocyclic compound thiazan,  $S<\begin{array}{l}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{array}>NH$, the sulphur analogue of morpholine,



$$O<\begin{array}{l}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{array}>NH.$$

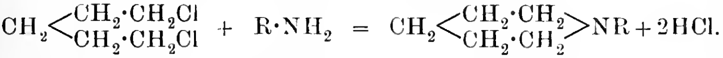
As this belongs to a new class of compounds, it has been considered advisable to describe independently the experiments connected with the formation and properties of these substances.

Alkylthiazans can readily be prepared by the interaction of ββ′-dichloroethyl sulphide and primary amines:



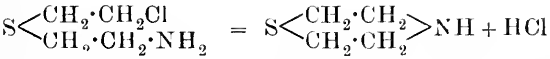
$$S<\begin{array}{l}CH_2\cdot CH_2Cl\\CH_2\cdot CH_2Cl\end{array} + R\cdot NH_2 = S<\begin{array}{l}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{array}>NR + 2HCl,$$

the reaction following a course analogous to the formation of derivatives of piperidine from αε-dichloropentane:



$$CH_2<\begin{array}{l}CH_2\cdot CH_2Cl\\CH_2\cdot CH_2Cl\end{array} + R\cdot NH_2 = CH_2<\begin{array}{l}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{array}>NR + 2HCl.$$

An attempt to prepare the parent thiazan according to the scheme:



$$S<\begin{array}{l}CH_2\cdot CH_2Cl\\CH_2\cdot CH_2\cdot NH_2\end{array} = S<\begin{array}{l}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{array}>NH + HCl$$

has recently been described by Gabriel and Colman (*Ber.*, 1912, **45**, 1644), in which no trace of the cyclic base was produced. It is noteworthy that in the experiments here described the yields of thiazan derivative varied from 40 to 60 per cent., in contrast with the practically theoretical yields of piperidines obtainable from αε-dichloropentane. It would thus appear that the presence of a sulphur atom in the chain tends to diminish the normal ring-forming capacity of the molecule containing chlorine atoms situated in the 1:5-positions. In all cases the thiazan was accompanied by a considerable proportion of a basic product of less volatility; the nature of this by-product was not investigated, but there can be little doubt that it is formed by a more complex reaction between the primary amine and the dichloroethyl sulphide.

The starting substance, ββ′-dichloroethyl sulphide, was prepared by V. Meyer (*Ber.*, 1886, **19**, 3259) by allowing ethylenechlorohydrin to react with aqueous potassium sulphide, and treating the resulting thiodiglycol with phosphorus trichloride:

$$K_2S+2CH_2Cl\cdot CH_2\cdot OH \longrightarrow S{<}\begin{matrix}CH_2\cdot CH_2\cdot OH\\ CH_2\cdot CH_2\cdot OH\end{matrix} \longrightarrow S{<}\begin{matrix}CH_2\cdot CH_2Cl\\ CH_2\cdot CH_2Cl\end{matrix}$$

The present author has found that the conversion of the glycol into its dichloride can be effected rapidly and quantitatively by warming a solution of thiodiglycol in concentrated hydrochloric acid on the water-bath.

As stated by V. Meyer, $\beta\beta'$-dichloroethyl sulphide is intensely poisonous, inflicting painful wounds, which heal only with the greatest difficulty, when brought into contact with the skin. That its action is toxic, and not merely irritative, as is the case with acids, is shown by the absence of pungency in the odour and by the fact that it takes effect only after some hours have elapsed. It can, nevertheless, be handled with perfect safety, provided that care is taken not to inhale its vapour or to allow it to come into contact with the skin.

In the present communication the methyl, ethyl, *iso*amyl, and benzyl derivatives of thiazan are described. They form strongly basic oils of characteristic odours reminiscent of those of alkylpiperidines of higher molecular weight, although more unpleasant. The methyl and ethyl derivatives are soluble in water, and may be separated from their aqueous solutions by the addition of alkali hydroxide. The lower members are volatile with steam. Their boiling points lie higher than those of the corresponding derivatives of piperidine and morpholine, as the following table shows:

	Methyl.	Ethyl.	Benzyl.
Piperidine ...	107°	129°	119°/13 mm.
Morpholine ...	115—116°	138—139°	128—129°/13 mm.
Thiazan	163—164°	184°	154°/13 mm.

They yield crystalline picrates, which are sparingly soluble in alcohol, and aqueous solutions of their hydrochlorides give with platinic chloride buff precipitates, which are insoluble in any liquid tried, with the exception of concentrated hydrochloric acid, which appears to decompose them. A peculiarity common to three of the four members of the series examined, namely, the methyl, ethyl, and *iso*amyl derivatives, is that the composition of these platinichlorides corresponds with the formula $(BH)PtCl_5$, instead of the usual $(BH)_2PtCl_6$, where B represents 1 molecule of the base. This may perhaps be attributed to the formation of derivatives of quadrivalent sulphur of the type ${>}S{<}\begin{matrix}Cl\\ Pt^{IV}\end{matrix}$, analogous to those produced by the action of mercuric chloride on sulphides:

$${>}S{<}\begin{matrix}Cl\\ Hg^{II}\end{matrix}$$

Benzylthiazan, on the other hand, forms a normal platinichloride, $(BH)_2PtCl_6$. No reason is apparent to account for this difference. The general properties of this salt are also somewhat different. The salts $(BH)PtCl_5$ are amorphous or only vaguely crystalline precipitates, which separate from the solution after some minutes. They are absolutely insoluble in alcohol, and possess no melting point. Benzylthiazan platinichloride appears instantaneously as a precipitate, apparently in the form of solidified drops of oil, and melts and decomposes at 172—174°; in fact, if a sample, slightly moist with a trace of alcohol, is placed in the steam-oven, it melts with evolution of gas. It differs further from the others in being sparingly soluble in alcohol, and sets to a resin when boiled with this solvent.

Mercuric chloride yields with aqueous solutions of thiazans a white, curdy precipitate, which rapidly becomes yellow.

Experiments are in progress with a view to the preparation of the parent substance thiazan.

EXPERIMENTAL.

ββ'-Dichloroethyl Sulphide.

Ethylenechlorohydrin (80 grams) was gradually added to a 50 per cent. aqueous solution of 280 grams of colourless sodium sulphide. The mixture rapidly became warm, and required to be cooled in order to prevent boiling. This was then warmed for two hours on the water-bath, cooled, and faintly acidified with hydrochloric acid. The potassium chloride was removed and washed with alcohol, and the filtrate evaporated to dryness under diminished pressure. The residue was extracted with alcohol, and the alcoholic solution again evaporated. The syrupy residue, consisting of thiodiglycol, was dissolved in 400 to 500 c.c. of concentrated hydrochloric acid, by which a deep red solution was formed. On warming this solution on the water-bath, after a few minutes the red colour was discharged, and the liquid became turbid owing to the separation of the oily dichloroethyl sulphide. After thus warming for an hour, the mixture was distilled in a current of steam until no more oil passed over. The distillate was twice extracted with chloroform, and the united chloroform extracts dried with calcium chloride and distilled, first on the water-bath, and afterwards on the oil-bath under diminished pressure. After removal of the chloroform almost the entire quantity passed over at 98°/10 mm. The yield was 74·5 grams, or 94 per cent. of the theoretical quantity obtainable from the ethylenechlorohydrin. In another preparation the product boiled constantly at 108°/14 mm. The boiling point under atmospheric pressure was 217°, corresponding with that recorded by Meyer, but decomposition was considerable at that temperature.

The odour of the oil is not unlike that of αε-dichloropentane, but is far more unpleasant. Its dangerously poisonous nature has already been mentioned.

4-*Methyl*-1:4-*thiazan*.

A mixture of 18 grams of anhydrous sodium acetate, 12 grams of a 33 per cent. solution of methylamine in alcohol, 17 grams of dichloroethyl sulphide, and about 20 c.c. of absolute alcohol were shaken in steam in a sealed tube for eight hours. The sodium chloride was removed and washed with alcohol, the filtrate being rendered strongly acid with dilute phosphoric acid, and evaporated nearly to dryness on the water-bath. Water was then added, and a neutral oil, which floated on the surface, was removed by extraction with ether. This oil, which amounted to about 1 c.c., possessed properties ascribable to the diacetate of thiodiglycol, but was not further investigated. After vigorously boiling the acid solution, in order to expel volatile impurities, excess of alkali was added, and the base driven over with steam, until the distillate showed no separation of oil on saturating a sample with alkali. A considerable quantity of brown, non-volatile oil remained with the solution in the flask. The total distillate, amounting to about 25 c.c., was then saturated with potassium hydroxide, and the oil separated. This was dried by boiling with solid potassium hydroxide, and distilled over metallic sodium. After distilling off the slight excess of methylamine dissolved in the oil, almost the entire quantity passed over between 163° and 164°/757 mm. as a colourless liquid with a characteristic odour, completely miscible with water or organic solvents. It is a powerful base, and fumes in the presence of acid vapours:

0·1739 gave 0·3269 CO_2 and 0·1573 H_2O. C=51·2; H=10·0.

$C_5H_{11}NS$ requires C=51·3; H=9·4 per cent.

The following constants were determined:

$$D_4^{15}\ 0{\cdot}99596,\ D_4^{20}\ 0{\cdot}99244,\ n_\alpha^{20^\circ}\ 1{\cdot}50176,\ n_\gamma^{20}\ 1{\cdot}52182.$$

The *hydrochloride*, precipitated as a white, crystalline mass on adding alcoholic hydrogen chloride to an ethereal solution of the base, collecting, washing well with ether, and drying at 78° in a vacuum over phosphoric oxide, melted sharply and almost without decomposition at 239° (uncorr.) after shrinking at 236°:

0·3057 required 39·6 c.c. $N/20$-$AgNO_3$. Cl=23·0.

$C_5H_{11}NS,HCl$ requires Cl=23·1 per cent.

The *platinichloride* separated as a buff, amorphous precipitate after some minutes on adding platinic chloride to a dilute solution of the base in dilute aqueous hydrochloric acid. Separation was complete only after the lapse of some hours, and filtration was extremely difficult. The substance was well washed with water and absolute alcohol, dried in the steam-oven, and subsequently in a vacuum over sulphuric acid. It decomposed at a high temperature without melting:

0·0694 gave 0·0276 Pt. Pt=39·8.
$C_5H_{11}NS,HPtCl_5$ requires Pt=39·8 per cent.

The *picrate* is immediately precipitated in a crystalline condition from even very dilute alcoholic solutions of the base on addition of picric acid in alcohol. It is very soluble in hot acetone, and can best be recrystallised by gradually adding acetone to a suspension in boiling absolute alcohol until complete solution takes place. It forms bright yellow needles, melting sharply with decomposition at 226° (uncorr.):

0·2463 gave 0·1690 $BaSO_4$. S=9·42.
$C_5H_{11}NS,C_6H_4O_7N_3$ requires S=9·25 per cent.

4-*Ethyl*-1:4-*thiazan*.

This was prepared in exactly the same manner as methylthiazan, from a mixture of 18 grams of sodium acetate, 16 grams of a 33 per cent. alcoholic solution of ethylamine, 17 grams of dichloroethyl sulphide, and about 15 c.c. of alcohol. The main product is a colourless basic oil, which after refractionation boils constantly at 184°/763 mm.; it is soluble in water, and closely resembles methylthiazan:

0·0923 gave 0·1851 CO_2 and 0·0922 H_2O. C=54·7; H=11·1.
$C_6H_{13}NS$ requires C=55·0; H=9·9 per cent.

The following constants were determined:

D_4^{15} 0·99295, D_4^{20} 0·98854, n_α^{20} 1·50180, n_γ^{20} 1·52065.

The *hydrochloride* melts sharply at 188° (uncorr.), almost without decomposition:

0·2846 required 34·1 c.c. $N/20$-$AgNO_3$. Cl=21·2.
$C_6H_{13}NS,HCl$ requires Cl=21·2 per cent.

The *platinichloride* closely resembles that obtained from methylthiazan, with the difference that it is vaguely crystalline, and can be more readily collected and washed. It decomposes indistinctly at about 222°:

0·0924 gave 0·0352 Pt. Pt = 38·1.

0·1549 „ 0·0596 Pt and 0·2130 AgCl (by combustion*). Pt = 38·5; Cl = 34·0.

$C_6H_{13}NS,HPtCl_5$ requires Pt = 38·7; Cl = 35·2 per cent.

[$(C_6H_{13}NS)_2,H_2PtCl_5$ „ Pt = 29·0; Cl = 31·7 „ „]

The *picrate* crystallises from a mixture of alcohol and acetone in yellow needles, melting at 185—186° (uncorr.) after shrinking at 178—180°:

0·2664 gave 0·1729 $BaSO_4$. S = 8·91.

$C_6H_{13}NS,C_6H_4O_7N_3$ requires S = 8·89 per cent.

4-iso*Amyl*-1:4-*thiazan.*

A mixture of 10 grams of *iso*amylamine, 15 grams of dichloroethyl sulphide, 10 grams of anhydrous sodium acetate, and 11 grams of finely-powdered anhydrous sodium carbonate was heated with about 100 c.c. of alcohol for three hours, with occasional agitation, on the water-bath under reflux. The sodium chloride and unchanged sodium carbonate were filtered off, and the bulk of the alcohol removed from the filtrate by distillation on the water-bath. The residue was treated with ether and dilute alkali, and the ethereal solution shaken with dilute sulphuric acid. The acid solution was then rendered alkaline, when the basic products separated as an oil. This was extracted with ether, the ethereal solution dried with potassium hydroxide, and the ether distilled off. The residue was distilled under diminished pressure on the oil-bath. After some unchanged *iso*amylamine had passed over, the temperature rapidly rose to 100°, and an oil distilled between 103° and 112°/13 mm. A considerable quantity of a brown, viscous residue remained in the flask. After three refractionations, a product boiling at 105—106°/13 mm. was obtained as a colourless oil, almost insoluble in water, and possessing the characteristic odour of thiazans:

0·1167 gave 0·2632 CO_2 and 0·1186 H_2O. C = 61·6; H = 11·3.

$C_9H_{19}NS$ requires C = 62·4; H = 11·0 per cent.

The *hydrochloride* melts sharply at 224° (uncorr.) almost without decomposition:

0·2323 required 22·0 c.c. *N*/20-$AgNO_3$. Cl = 16·8.

$C_9H_{19}NS,HCl$ requires Cl = 16·9 per cent.

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* The author hopes shortly to describe a method for the determination of halogens in organic compounds by combustion in oxygen. An estimation of chlorine by the Carius method was carried out, but was most unsatisfactory, owing to the deposition of platinum with the silver chloride:

0·1369 gave 0·1794 AgCl. Cl = 32·3.

The *platinichloride* resembles that obtained from methylthiazan, except that it is more rapidly precipitated from solution:

0·1494 gave 0·0530 Pt. Pt=35·5.

$C_9H_{19}NS,HPtCl_5$ requires Pt=35·7 per cent.

The *picrate* forms bright yellow needles, which melt sharply at 147° without decomposition:

0·2351 gave 0·1359 $BaSO_4$. S=7·94.

$C_9H_{19}NS,C_6H_4O_7N_3$ requires S=7·96 per cent.

4-*Benzyl*-1:4-*thiazan*.

This was prepared in the same way as the *iso*amyl derivative; from a mixture of 10 grams of benzylamine, 14 grams of dichloroethyl sulphide, 9 grams of sodium acetate, and 12 grams of sodium carbonate, heated with 100 c.c. of alcohol for four hours on the water-bath under reflux.

The fraction passing over between 153° and 157°/13 mm. was collected separately and redistilled. It formed a colourless oil boiling at 154°/13 mm., insoluble in water, but soluble in organic liquids:

0·1088 gave 0·2705 CO_2 and 0·0822 H_2O. C=67·8; H=8·4.
0·1688 ,, 0·2083 $BaSO_4$. S=16·8.

$C_{11}H_{15}NS$ requires C=68·4; H=7·8; S=16·6 per cent.

The following constants were determined:

D^{15}_{4} 1·08328, D^{20}_{4} 1·07876, n^{20}_{α} 1·56605, n^{20}_{γ} 1·60347.

The *hydrochloride* melts sharply at 225° (uncorr.):

0·2266 required 19·6 c.c. *N*/20-$AgNO_3$. Cl=15·3.

$C_4H_{15}NS,HCl$ requires Cl=15·4 per cent.

The *platinichloride* appears immediately as an amorphous, buff precipitate, which is sparingly soluble in alcohol, but cannot well be recrystallised from this solvent, as it softens to an intractable resin in contact with boiling alcohol. It melts and decomposes at 172—174°, after softening at 140°. A sample slightly contaminated with alcohol softened to a spongy mass, which subsequently solidified, when placed in the steam-oven:

0·0612 gave 0·0149 Pt. Pt=24·3.

$(C_{11}H_{15}NS)_2,H_2PtCl_6$ requires Pt=24·5 per cent.

The *picrate* is even less soluble in hot alcohol than the picrates of the other derivatives examined, and required a larger proportion of acetone for recrystallisation. It forms small, blunt, light yellow prisms, melting at 218° (uncorr.) to a dark liquid:

0·1890 gave 0·1043 $BaSO_4$. S=7·58.

$C_{11}H_{15}NS,C_6H_4O_7N_3$ requires S=7·60 per cent.

Finally, it may be mentioned that the basic by-products of higher boiling point which occur during the formation of the alkyl thiazans are incapable of forming picrates in alcoholic solution. This fact has been utilised in one or two preparations to separate the pure thiazan from impure fractions. The picrates may be decomposed with concentrated hydrochloric acid, and the free base liberated by means of excess of alkali.

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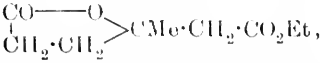
UNIVERSITY OF BERLIN.

CLXXI.—*β-Hydroxy-αβ-dimethyladipic Acid and β-Hydroxy-ααβ-trimethyladipic Acid.*

By VICTOR JOHN HARDING.

THE work described in this communication was carried out some years ago, and as the opportunities of continuing this research in the near future seem limited, it has been judged advisable to place on record the results so far obtained. It was hoped at the commencement of this research that β-hydroxy-αβ-dimethyladipic and β-hydroxy-ααβ-trimethyladipic acids would prove of value in synthetical work on the terpenes. Indeed, the latter acid has already been partly investigated from this point of view by Blaise (*Compt. rend.*, 1900, **130**, 1033), who pointed out the extreme readiness with which it underwent lactone formation, and its subsequent stability. The author's results in the main confirm those of Blaise, but one or two of the reactions which it undergoes are of interest in themselves.

Both acids were prepared by the condensation of ethyl lævulate and the corresponding α-bromo-esters by means of zinc. Duden and Freydag (*Ber.*, 1903, **36**, 953) condensed ethyl lævulate and ethyl bromoacetate by means of zinc, and obtained the ethyl ester of the lactone of β-hydroxy-β-methyladipic acid,



$$\begin{array}{l}\mathrm{CO{-\!-}O}\\ \mathrm{CH_2{\cdot}CH_2}\end{array}\!\!>\mathrm{CMe{\cdot}CH_2{\cdot}CO_2Et},$$

in 30—40 per cent. yields. Blaise by a similar condensation of methyl lævulate and methyl α-bromo*iso*butyrate obtained the methyl ester of the lactone of β-hydroxy-ααβ-trimethyladipic acid,

$$\begin{array}{l}\mathrm{CO{-\!-}O}\\ \mathrm{CH_2{\cdot}CH_2}\end{array}\!\!>\mathrm{CMe{\cdot}CMe_2{\cdot}CO_2Me},$$

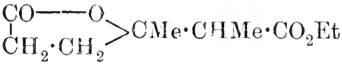
in yields of 15—17 per cent. In neither case was there isolated any of the corresponding hydroxy-ester.

The formation of lactones from esters of lævulic acid by the Barbier-Grignard reagent is well known (compare Grignard, *Compt. rend.*, 1902, **139**, 639; Jones and Tattersall, Trans., 1904, **85**, 1691).

If the Reformatsky reaction between ethyl lævulate and ethyl α-bromopropionate is carried out in benzene solution, excellent yields are obtained of a condensation product, which consists of a mixture of diethyl β-hydroxy-αβ-dimethyladipate (I) and the ethyl ester of the lactone of β-hydroxy-αβ-dimethyladipic acid (II),

$CO_2Et\cdot CHMe\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CO_2Et$

(I.)



$$\begin{array}{l} CO—O \\ | \\ CH_2\cdot CH_2 \end{array}\!\!>CMe\cdot CHMe\cdot CO_2Et$$

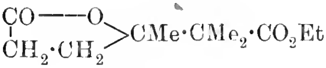
(II.)

the use of the benzene as a diluent evidently hindering the formation of lactone.

A similar mixture of hydroxy-ester (III) and lactone (IV) is obtained by the condensation of ethyl lævulate and ethyl α-bromoisobutyrate by means of zinc in benzene solution, the yields being 70—80 per cent., whereas Blaise, using the methyl esters without the use of any diluent, obtained only the lactone in very poor yields. A redistillation of the products of reaction has no effect on the proportion of hydroxy-ester and lactone present.

$CO_2Et\cdot CMe_2\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CO_2Et$

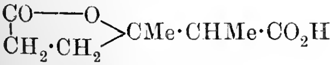
(III.)



$$\begin{array}{l} CO—O \\ | \\ CH_2\cdot CH_2 \end{array}\!\!>CMe\cdot CMe_2\cdot CO_2Et$$

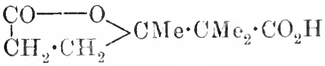
(IV.)

The acid hydrolysis of these mixtures of hydroxy-esters and lactones yields the corresponding acid lactones, the condensation mixture from α-bromopropionic acid giving the lactone of β-hydroxy-αβ-dimethyladipic acid (V), and that from α-bromoisobutyric acid furnishing the lactone of β-hydroxy-ααβ-trimethyladipic acid (VI):



$$\begin{array}{l} CO—O \\ | \\ CH_2\cdot CH_2 \end{array}\!\!>CMe\cdot CHMe\cdot CO_2H$$

(V.)



$$\begin{array}{l} CO—O \\ | \\ CH_2\cdot CH_2 \end{array}\!\!>CMe\cdot CMe_2\cdot CO_2H$$

(VI.)

Both acids crystallise well from dry ether. The author, however, is unable to confirm Blaise's statement that hydrolysis by means of alkali completely decomposes the ester of the lactone of β-hydroxy-ααβ-trimethyladipic acid into lævulic and isobutyric acids. The alkaline hydrolysis of the mixed hydroxy-ester and lactone yields β-hydroxy-ααβ-trimethyladipic acid, which can be distilled with the production of only a small amount of the acid lactone. The decomposition of β-hydroxy-ααβ-trimethyladipic acid into lævulic and *iso*butyric acids, however, was observed if the acid was distilled in a rapid current of steam in the presence of 20 per cent. sulphuric acid.

Attempts to prepare β-bromo-ααβ-trimethyladipic acid were unsuccessful. The action of aqueous hydrobromic acid saturated at 0° on diethyl β-hydroxy-ααβ-trimethyladipate (III) yielded only the lactone of β-hydroxy-ααβ-trimethyladipic acid (VI). The successive actions of phosphorus pentabromide, ethyl alcohol, and diethylaniline on diethyl β-hydroxy-ααβ-trimethyladipate resulted in the formation of the ethyl ester of the lactone of β-hydroxy-ααβ-trimethyladipic acid (IV). The formation of the lactone instead of the expected unsaturated ester by this method is interesting.

EXPERIMENTAL.

Condensation of Ethyl Laevulate and Ethyl-α-bromopropionate: Diethyl β-Hydroxy-αβ-dimethyladipate (I).

Fifteen grams of ethyl lævulate were mixed with 17 grams of ethyl α-bromopropionate dissolved in twice the volume of dry benzene, and 7 grams of zinc added. The commencement of the reaction was aided by a little iodine and by heating on the water-bath, but when once begun was extremely vigorous, and it was necessary to resort to cooling. The reaction was complete at about the end of two hours, nearly all the zinc having been dissolved. The gelatinous, yellow product was decomposed by ice and dilute hydrochloric acid, extracted with ether, the ethereal extract washed several times with water, dried, and distilled under a pressure of 18 mm. The chief fraction was found to boil at 160—170°, the yield being 70 per cent. The portion boiling at 166° was used for analysis:

0·1020 gave 0·2210 CO_2 and 0·0769 H_2O. C=59·1; H=8·3.
$C_{12}H_{22}O_5$ requires C=58·8; H=8·9 per cent.
$C_{10}H_{16}O_4$,, C=60·0; H=8·0 ,, ,,

The results indicate that the condensation product is a mixture of diethyl β-hydroxy-αβ-dimethyladipate and the corresponding lactone.

Lactone of β-Hydroxy-αβ-dimethyladipic Acid (V).

The diethyl β-hydroxy-αβ-dimethyladipate obtained from the previously described Reformatsky reaction was hydrolysed by heating on the water-bath for six hours with concentrated hydrochloric acid, and then pouring into water. The acid was obtained from the aqueous solution by extraction with ether, the ethereal extract dried, and the ether removed by evaporation, when an oil remained, which rapidly solidified. The adhering oil was removed from the crystals by absorption by porous porcelain, and the acid purified by crystallisation from dry ether, from which it separates in large, stout prisms melting at 98°:

0·1341 gave 0·2702 CO_2 and 0·0845 H_2O. C=55·6; H=7·0.

$C_8H_{12}O_4$ requires C=55·8; H=7·0 per cent.

0·2104 required for neutralisation 0·0484 NaOH.

A monobasic acid, $C_8H_{12}O_4$, requires 0·0489 NaOH.

After being boiled for twenty minutes with excess of *N*/10-sodium hydroxide:

0·2104 required 0·0992 NaOH.

A lactonic acid, $C_8H_{12}O_4$, requires 0·0978 NaOH.

All attempts to prepare an ester of the lactonic acid by direct esterification were unsuccessful.

*Condensation of Ethyl Laevulate and Ethyl α-Bromo*iso*butyrate: Diethyl β-Hydroxy-ααβ-trimethyladipate* (III).

This condensation was carried out in a manner exactly similar to that described in the preparation of its lower homologue. It is an almost colourless, odourless oil, boiling at 171—175°/18 mm. Analysis shows that, like its lower homologue, it is a mixture of the hydroxy-ester and the ester of the acid lactone:

I. 0·1621 gave 0·3585 CO_2 and 0·1241 H_2O. C=60·3; H=8·5.

II. (Redistilled) 0·1485 gave 0·3302 CO_2 and 0·1140 H_2O. C=60·6; H=8·5.

$C_{13}H_{24}O_5$ requires C=60·0; H=9·2 per cent.

$C_{11}H_{18}O_4$ „ C=61·7; H=8·5 „ „

β-Hydroxy-ααβ-trimethyladipic Acid,
$CO_2H·CMe_2·CMe(OH)·CH_2·CH_2·CO_2H$.

The hydroxy-acid is prepared by the alkaline hydrolysis of ethyl β-hydroxy-ααβ-trimethyladipate. The diethyl ester was heated for half an hour with alcoholic potassium hydroxide. The solution was then diluted with water, and the alcohol removed by evaporation.

The alkaline liquid was acidified with dilute hydrochloric acid until it just showed an acid reaction towards Congo-red, and immediately extracted by means of ether. The ethereal extract was dried, the ether removed by evaporation, and the residual oil very rapidly distilled under diminished pressure. In this way the acid was obtained as a yellow oil, which did not crystallise. An analysis showed that it consisted chiefly of free hydroxy-acid:

0·1340 gave 0·2560 CO_2 and 0·0900 H_2O. C=52·1; H=7·5.

$C_9H_{16}O_5$ required C=52·9; H=7·8 per cent.

A determination of the basicity showed that it contained a small amount of lactone:

0·1503 required for neutralisation 0·0432 NaOH.

A dibasic acid, $C_9H_{16}O_5$, requires 0·0589 NaOH.

After being boiled with excess of *N*/10-sodium hydroxide:

0·1503 required 0·0590 NaOH.

Decomposition of β-Hydroxy-ααβ-trimethyladipic Acid: Production of Laevulic and iso*Butyric Acids.*

Five grams of the oily β-hydroxy-ααβ-trimethyladipic acid were mixed with five times the volume of 20 per cent. sulphuric acid, and submitted to distillation in a rapid current of steam. An oil distilled over, which was identified as *iso*butyric acid by ether extraction, distillation, and analysis. (Found, C=54·1; H=9·3. Calc., C=54·5; H=9·1 per cent.) The residue from the steam distillation on repeated extraction with ether yielded lævulic acid.

Ethyl Ester of the Lactone of β-Hydroxy-ααβ-trimethyladipic Acid (IV).

This ester was prepared by Blaise by the interaction of the silver salt of the acid lactone and ethyl iodide. It can also be prepared in a pure state by gently heating on the water-bath equimolecular amounts of impure diethyl β-hydroxy-ααβ-trimethyladipate and phosphorus pentabromide. The resulting product was cooled, poured into ethyl alcohol, allowed to remain for some time, and the alcoholic solution poured into water. The oil which separated was extracted with ether, the ether evaporated, and the residue, without any further purification, boiled for four hours with twice its volume of diethylaniline. The resulting solution was then poured into dilute hydrochloric acid, and the lactone ester extracted by means of ether and distilled. The ester is a colourless oil boiling at 165—168°/18 mm. (Found, C=61·6; H=8·2. $C_{11}H_{14}O_4$ requires C=61·7; H=8·4 per cent.)

Lactone of β-Hydroxy-ααβ-trimethyladipic Acid (VI).

This lactone was produced by the action of an aqueous solution of hydrogen bromide saturated at 0° on diethyl β-hydroxy-ααβ-trimethyladipate by gentle heating on a water-bath for about four hours. At the end of this time the product was poured into water, and the acid extracted by means of ether. On removal of the ether the residual oil crystallised. The acid was freed from adhering oil by means of porous porcelain and purified by recrystallisation from dry ether. It crystallises in large, colourless prisms, melting at 108—109°:

0·1180 gave 0·2495 CO_2 and 0·0792 H_2O. C=57·6; H=7·5.
$C_9H_{14}O_4$ requires C=58·0; H=7·5 per cent.

0·2372 required for neutralisation 0·0496 NaOH.
A monobasic acid, $C_9H_{14}O_4$, requires 0·0510 NaOH.

After being boiled with excess of $N/10$-sodium hydroxide:

0·2372 required 0·1022 NaOH.
A lactonic acid, $C_9H_{14}O_4$, requires 0·1020 NaOH.

This work was carried out in the chemical laboratories of the University of Manchester, and the author desires to express his acknowledgment to Prof. W. H. Perkin, jun.

McGill University,
Montreal.

CLXXII.—*iso*Quinoline Derivatives. Part VII. The Preparation of Hydrastinine from Cotarnine.

By Frank Lee Pyman and Frederic George Percy Remfry.

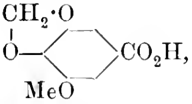
In the course of the last few years it has frequently been observed by different investigators that derivatives of pyrogallol trimethyl ether under the reducing influence of sodium and alcohol suffer the replacement of one or even two methoxyl groups by hydrogen.

Thus, Kostanecki and Lampe (*Ber.*, 1908, **41**, 1327) obtained a 3:5-dimethoxyphenyl derivative in the place of an expected 3:4:5-trimethoxyphenyl compound; Semmler (*Ber.*, 1908, **41**, 1774) found that gallic acid trimethyl ether gave rise to *m*-methoxybenzoic acid:

and that *iso*elemicin (*Ber.*, 1908, **41**, 2556) gave 3:5-dimethoxypropylbenzene:

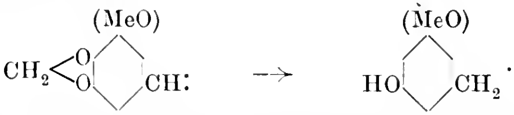
and recently Thoms and Siebeling (*Ber.*, 1911, **44**, 2134) have shown that pyrogallol trimethyl ether itself yields, on reduction with sodium and alcohol, resorcinol dimethyl ether:

In the case of derivatives of pyrogallol methyl methylene ether, however, no instance of the displacement of the methoxyl group by hydrogen has hitherto been recorded. Semmler (*loc. cit.*) attempted the replacement of the methoxyl group in myristicinic acid,



by means of sodium and alcohol, but recovered the acid unchanged.

On the other hand, another change involving the methylenedioxy-group has been observed in the reduction of methylenedioxy- and methylenedioxy-methoxy-compounds by means of sodium and alcohol (Ciamician and Silber, *Ber.*, 1890, **23**, 1162; Thoms, *Ber.*, 1903, **36**, 3449), or sodium amalgam in alkaline solution (Salway, Trans., 1910, **97**, 2413). This change has hitherto only been observed in the case of compounds containing the methylenedioxy-group in the 3:4-position with relation to an unsaturated carbon atom in the 1-position, and results in the replacement of the 3:4-methylenedioxy-group by a hydroxy-group in the 3-position, and a hydrogen atom in the 4-position:



With these facts before us, we decided to study the action of sodium and alcohol on hydrocotarnine (I) with the hope that the

(I.) (II.)

methoxy-group would be displaced by hydrogen, giving rise to hydrohydrastinine (II). The investigation has shown that the reaction does indeed proceed mainly in the desired direction, hydrohydrastinine being produced in a yield amounting to about 40 per cent. of the theoretical when either absolute alcohol or dry fusel oil (b. p. 122—132°) is employed. At the same time, however, a mixture of phenolic bases produced by the reduction and fission of the methylenedioxy-groups of hydrocotarnine and hydrohydrastinine is obtained in small yield.

This reaction is of considerable interest from the economic point of view for the following reasons:

Hydrocotarnine may be prepared in almost quantitative yield by reducing cotarnine with sodium amalgam in mineral acid solution —a method used by Freund and Dormeyer (*Ber.*, 1891, **24**, 2734) for the reduction of hydrastinine to hydrohydrastinine—and cotarnine is readily obtained by oxidising narcotine, which is a by-product in the preparation of morphine from opium, and is comparatively cheap. Hydrohydrastinine is therefore now rendered accessible in quantity, and Freund and Will (*Ber.*, 1887, **20**, 2403) have previously shown that this alkaloid, when oxidised with sulphuric acid and potassium dichromate, yields hydrastinine. The latter base, which finds application in medicine, has hitherto (or until quite recently: compare Decker, *Chem. Zeit.*, 1911, **35**, 1077; Freund, D.R.-P. 241136) been prepared by the oxidation of the very costly alkaloid hydrastine.

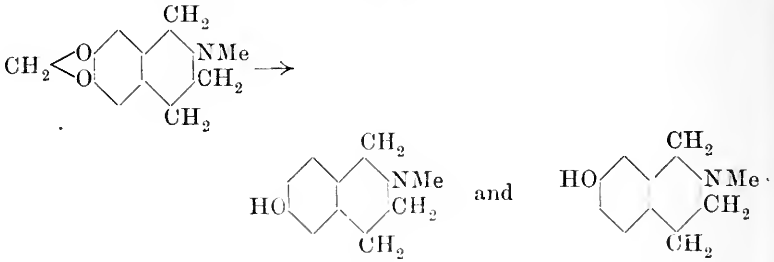
The preparation of hydrastinine from narcotine is therefore of some importance, the more so in view of the recent work by Hope and Robinson (Proc., 1912, **28**, 17), which seems to indicate that the synthesis of *l*-hydrastine itself from hydrastinine may shortly be effected. Up to the present, however, the transformations effected may be represented as follows:

$$\begin{tikzcd}
\text{Narcotine} \arrow[r, "\text{Oxidation}"] & \text{Cotarnine} \arrow[r, "\text{Reduction}"] & \text{Hydrocotarnine} \arrow[d, "\text{Reduction}"] \\
dl\text{-}\beta\text{-(or }\alpha\text{-)Hydrastine} & \text{Hydrastinine} \arrow[l] & \text{Hydrohydrastinine.} \arrow[l, "\text{Oxidation}"']
\end{tikzcd}$$

Direct transformation of narcotine into hydrastine or cotarnine into hydrastinine by treatment with sodium and alcohol was not to be expected by reason of the known properties of these compounds, but it has been found that cotarnine itself yields a small amount of hydrohydrastinine when treated in this way.

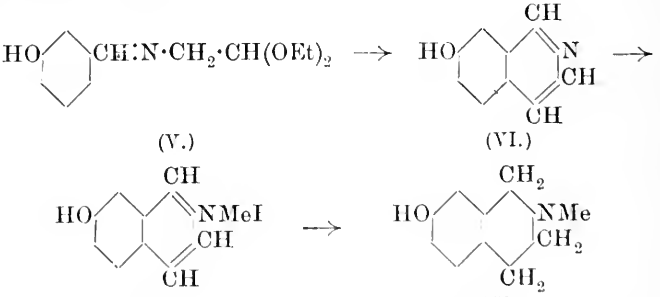
In the preparation of hydrohydrastinine from hydrocotarnine a mixture of phenolic bases, amounting after purification to about 5 per cent. of the hydrocotarnine employed, is obtained as a by-product. By means of methods fully described in the experimental part of this paper, four individual phenolic bases have been isolated from this mixture in a pure state. Two of these are isomeric hydroxy-2-methyltetrahydro*iso*quinolines, melting at 182—183° (corr.) and 171—172° (corr.) respectively, and it seemed probable that they were produced from the hydrohydrastinine previously formed.

A quantity of pure hydrohydrastinine was therefore treated with a large excess of sodium and fusel oil, when a mixture of these two bases resulted; it is clear from the latter mode of formation that these bases are 6-hydroxy-2-methyltetrahydro*iso*quinoline (III) and 7-hydroxy-2-methyltetrahydro*iso*quinoline (IV):



(III.) (IV.)

In order to discriminate between the two bases, 7-hydroxy-2-methyltetrahydro*iso*quinoline has been prepared in a manner which renders its constitution certain. Fritzsch (*Annalen*, 1895, **286**, 1) prepared 7-hydroxy*iso*quinoline (VI) by the internal condensation of *m*-hydroxybenzylideneaminoacetal (V), and carried out experiments to establish its constitution. By reducing the methiodide (VII) of this base, we have obtained 7-hydroxy-2-methyltetrahydro*iso*quinoline (VIII):

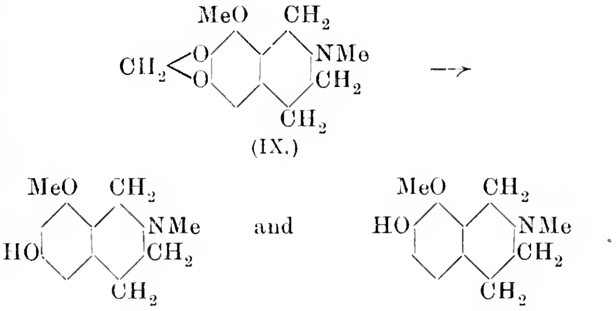


(VII.) (VIII.)

This base melts at 171—172° (corr.), and admixture with the base from hydrocotarnine, melting at 171—172° (corr.), does not change the melting point.

The base from hydrocotarnine melting at 171—172° (corr.) is therefore 7-hydroxy-2-methyltetrahydro*iso*quinoline, and its isomeride melting at 182—183° (corr.) is consequently 6-hydroxy-2-methyltetrahydro*iso*quinoline.

The other two phenolic bases isolated from the mixture are isomeric hydroxy-8-methoxy-2-methyltetrahydro*iso*quinolines, melting at 202—203° (corr.) and 163—164° (corr.) respectively, and there can be no doubt that they are formed by the reduction and fission of the methylenedioxy-group in hydrocotarnine in the same way that the two first-mentioned phenolic bases are produced from hydrohydrastinine:



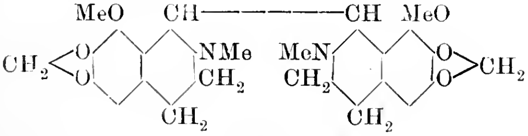
(IX.)

(X.) (XI.)

In order to discriminate between the two bases, small quantities of each have been hydrolysed to the corresponding dihydroxy-bases by means of concentrated hydrochloric acid at 160°, when the base melting at 202—203° (corr.) gave an amorphous hydrochloride giving no coloration with ferric chloride, whilst its isomeride melting at 163—164° (corr.) gave a crystalline hydrochloride affording the typical catechol reactions.

The base melting at 163—164° (corr.) is therefore 7-hydroxy-8-methoxy-2-methyltetrahydro*iso*quinoline (XI), and consequently the base melting at 202—203° (corr.) is 6-hydroxy-8-methoxy-2-methyltetrahydro*iso*quinoline (X).

The mother liquors from the crystallisation of hydrohydrastinine hydrobromide invariably afforded a quantity of bishydrocotarnine hydrobromide (XII), a compound which has been described by Freund and Reitz (*Ber.*, 1906, **39**, 2231):

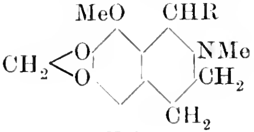


(XII.)

The occurrence of this substance in the reaction product is due to its presence as an impurity in the hydrocotarnine employed. The latter was prepared by reducing cotarnine in hydrochloric acid solution with sodium amalgam, and investigation has shown that a small amount of bishydrocotarnine can be isolated from it.

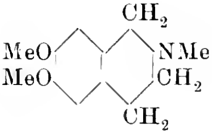
The results obtained in the case of hydrocotarnine have led us to test the action of sodium and alcohol on some allied bases.

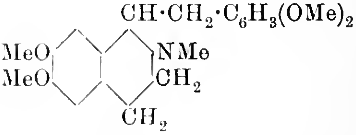
Attempts have been made to replace the methoxyl group by hydrogen in the case of certain 1-alkylhydrocotarnines (XIII) which have been described by Freund and Reitz (*loc. cit.*), but in every


(XIII.)

case unsuccessfully; thus 1-methyl-, 1-ethyl-, and 1-benzyl-hydrocotarnine are recovered for the greater part unchanged or only slightly impure after treatment with 1·5 parts of sodium and sufficient fusel oil—quantities which give a good yield of hydrohydrastinine from hydrocotarnine; in each case, however, traces of phenolic bases were produced.

6:7-Dimethoxy-2-methyltetrahydro*iso*quinoline (XIV) (Pyman, Trans., 1909, **95**, 1273) and *dl*-laudanosine (XV), which contain respectively one and two *o*-dimethoxy-groups, are recovered un-


(XIV.)


(XV.)

changed after treatment with sodium and fusel oil under similar conditions.

EXPERIMENTAL.

Hydrocotarnine.

The hydrocotarnine employed in this investigation was prepared by reducing cotarnine with sodium amalgam in dilute hydrochloric acid solution. A similar method was devised by Freund and Dormeyer (*Ber.*, 1891, **24**, 2734) for the reduction of hydrastinine to hydrohydrastinine. By the reduction of cotarnine in this way a quantitative yield of crude hydrocotarnine is obtained, but the product contains a small percentage (about 3 per cent.) of bishydrocotarnine. These bases may be separated by fractional crystallisation of the hydrobromides, but for the purpose of the following operations this process is superfluous and has not usually been adopted, since hydrohydrastinine hydrobromide and bishydrocotarnine hydrobromide can equally well be separated.

Pure hydrocotarnine crystallises from light petroleum in colourless plates which melt at 55·5—56·5° (corr.); its hydrobromide melts at 236—237° (corr.).

The Preparation of Hydrohydrastinine from Hydrocotarnine.

One hundred and twenty grams of hydrocotarnine were dissolved in 450 c.c. of dry fusel oil (b. p. 122—132°). One-third of this solution was placed in a 5-litre bolt-head, fitted with air condenser and dropping funnel, in an oil-bath maintained throughout at 130—135°, and 180 grams of sodium were added at once. As soon as the sodium had melted, the remaining two-thirds of the solution were run slowly on to it in the course of about twenty minutes, when the internal temperature rose to 155—160°. Dry fusel oil (b. p. 122—132°) was then run on to the sodium in a constant stream in quantities of 250 c.c. every ten minutes for another eighty to one hundred and twenty minutes, when nearly all the sodium dissolved, and the small, undissolved pieces were skimmed off. The internal temperature during this time gradually fell to 129°. The fusel oil was then cooled, mixed with 1 litre of water and 800 c.c. of commercial hydrochloric acid, and thoroughly shaken. The aqueous liquor was then removed, and the fusel oil extracted several times with dilute hydrochloric acid.

The aqueous liquor and extracts were then combined, rendered alkaline with sodium carbonate, and the base extracted with chloroform. The chloroform extract was washed with dilute aqueous sodium hydroxide to remove the phenolic bases, dried with potassium carbonate, and the solvent removed by distillation.

The chloroform residue consisting of crude hydrohydrastinine was dissolved in 300 c.c. of 95 per cent. alcohol, and slightly acidified by the addition of 30 per cent. hydrobromic acid, when, on keeping, 65—70 grams of hydrohydrastinine hydrobromide crystallised out; this was collected, washed with alcohol, and recrystallised from water. The salt was then dissolved in warm water, and mixed with aqueous sodium carbonate, when hydrohydrastinine was precipitated as an oil, which readily crystallised on cooling and scratching; after recrystallisation from light petroleum, it melted at 61—62° (corr.), and a specimen of hydrohydrastinine prepared by the reduction of hydrastinine obtained by the oxidation of hydrastine together with a mixture melted at the same temperature.

The identity of the hydrohydrastinine from hydrocotarnine was further established by analysis of the base (Found, C=68·9;

$H = 6{\cdot}8$. Calc., $C = 69{\cdot}1$; $H = 6{\cdot}8$ per cent.), and of the hydrobromide (Found, $C = 48{\cdot}7$; $H = 5{\cdot}3$. Calc., $C = 48{\cdot}5$; $H = 5{\cdot}2$ per cent.); the latter salt when pure melts at 293° (corr.). The hydrohydrastinine from hydrocotarnine readily gave hydrastinine, identical in all respects with that obtained by the oxidation of hydrastine, when oxidised by means of dilute sulphuric acid and potassium dichromate, as indicated by Freund and Will (*Ber.*, 1887, **20**, 2403).

Isolation of Bishydrocotarnine.

The alcoholic mother liquors from the hydrohydrastinine hydrobromide were evaporated sufficiently to remove the alcohol, diluted with 100 c.c. of water, and kept, when 6 to 8 grams of bishydrocotarnine hydrobromide separated in large, prismatic crystals, which melted and decomposed at 240° (corr.). [Found (in salt dried at 100°), $C = 48{\cdot}1$; $H = 5{\cdot}3$. Calc., $C = 47{\cdot}8$; $H = 5{\cdot}0$ per cent.]

A specimen of the base prepared from this salt crystallised from alcohol in square plates, which melted at 163—164° (corr.) (Found, $C = 65{\cdot}6$; $H = 6{\cdot}5$. Calc., $C = 65{\cdot}3$; $H = 6{\cdot}4$ per cent.), and gave an excellent yield of cotarnine on oxidation.

These properties of bishydrocotarnine are in accordance with those found by Freund and Reitz (*Ber.*, 1906, **39**, 2231) and Freund and Kupfer (*Annalen*, 1911, **384**, 1).

The final mother liquors remaining after the crystallisation of this salt contained a mixture of hydrohydrastinine and hydrocotarnine hydrobromides.

Separation of the Phenolic Bases.

The aqueous sodium hydroxide washings (p. 1601) of the chloroform solution of total bases contain the phenolic bases in a crude state; after slightly acidifying the liquor with hydrochloric acid, rendering alkaline with sodium carbonate, and extracting with chloroform, the crude bases are obtained as a viscid, dark brown, turbid gum. This product contains a large proportion of nearly black, resinous matter, and is purified as follows. It is dissolved in dilute hydrochloric acid, and extracted with ether to remove traces of fusel oil, then rendered strongly alkaline with sodium carbonate in a separator, when it separates as a dark brown gum. The mixture of liquor and gum is then thoroughly extracted with ether, which removes the purified phenolic bases, and these are obtained as a clear, pale brown gum in quantity amounting to about 5 per cent. of the hydrocotarnine employed.

It has already been explained in the introduction that this product contains the two isomeric 6(and 7)-hydroxy-2-methyltetrahydro*iso*quinolines (*A* and *B*) produced by the further action of the sodium and alcohol on hydrohydrastinine, together with the two isomeric 6(and 7)-hydroxy-8-methoxy-2-methyltetrahydro*iso*quinolines (*C* and *D*) produced from hydrocotarnine. The proportions in which each occur are somewhat variable, and the order in which the methods of separation are employed have to be suited to the particular batch.

When the purified phenolic bases are taken up in two volumes of ether and kept, a proportion—10—30 per cent.—separates in crystalline form. On occasions, this melts at 155—160°, and on recrystallisation readily yields the base *A* in pure form, melting at 182—183° (corr.); at other times, the crystalline fraction melts, for instance, at 140—150°, and does not then readily yield an individual base on fractional crystallisation.

The total purified phenolic bases (or the residue after the removal of *A*) were then dissolved in ten parts of 10 per cent. aqueous sodium hydroxide, and benzoylated by Schotten-Baumann's method, using 2 parts of benzoyl chloride; the benzoylated bases were then extracted with ether, shaken into dilute hydrochloric acid, regenerated by means of sodium carbonate, and again extracted with ether. The ethereal residue was then dissolved in hot dilute hydrobromic acid (using ten times its weight of water and sufficient 30 per cent. hydrobromic acid), when on keeping a quantity of a crystalline salt separated. This consisted either of the hydrobromide of the benzoyl derivative of *B* in a pure state, melting at 220°, or of a mixture melting at 190—210° of this salt with the hydrobromide of the benzoyl derivative of *D*; in the second case, the salts were separated by fractional crystallisation from water, when the last mentioned (m. p. 260°) separated first.

The mother liquors remaining after the removal of these salts deposited only oils sparingly soluble in water on further concentration; they were therefore treated with sodium carbonate, and the benzoyl bases extracted with ether. The benzoyl bases were then hydrolysed by boiling for a short time with 3 parts of alcohol and 3 parts of 10 per cent. aqueous sodium hydroxide, when, after removing the alcohol, neutralising the liquors with acid, and rendering alkaline with sodium carbonate, the corresponding phenolic bases were extracted with ether. After removing the solvent and mixing the resulting oil with an equal volume of ethyl acetate, crystals separated on keeping (mother liquor *M*). These on one occasion melted at 169°, and readily gave the base *A* (m. p. 182—183°) on crystallisation from ethyl acetate; on another occasion they melted at about 150°, and the melting point was little affected by recrystallising the substance from ethyl acetate; in this case the crystals were dissolved in dilute hydriodic acid (using 3 parts of water and sufficient concentrated acid), when, on cooling, the hydriodide of base *C* separated in a pure state, melting at 223°; on then regenerating the bases from the mother liquors and crystallising them from ethyl acetate, a quantity of the base *A* was obtained, and the mother liquors from this again afforded a small quantity of the hydriodide of *C*.

The mother liquor *M* still contained a very large proportion of the original purified phenolic bases, which were left on distillation of the solvent as a clear, light brown oil.

In order to give some idea of the quantities in which the various bases were isolated in a pure state, the following details are given:

Fifty-six grams of purified phenolic bases gave:

14·1 grams of 7-benzoyloxy-2-methyltetrahydro*iso*quinoline hydrobromide (derived from *B*).

3·0 grams of 6-hydroxy-2-methyltetrahydro*iso*quinoline (*A*).

1·7 grams of 6-hydroxy-8-methoxy-2-methyltetrahydro*iso*quinoline hydriodide (*C*).

Forty-five grams of purified phenolic bases gave:

21·0 grams of the mixed hydrobromides of the benzoyl derivatives of *B* and *D*, from which

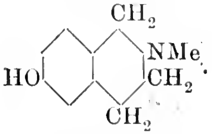
3·7 grams of 7-benzoyloxy-8-methoxy-2-methyltetrahydro*iso*quinoline hydrobromide (derived from *D*) were isolated in a pure state, the remainder consisting chiefly of 7-benzoyloxy-2-methyltetrahydro*iso*quinoline hydrobromide (derived from *B*).

3·0 grams of 6-hydroxy-2-methyltetrahydro*iso*quinoline (*A*).

Common Properties of the Phenolic Bases.

The properties of the four under-mentioned phenolic bases are very similar. All are insoluble in water or aqueous sodium carbonate, but readily soluble in dilute acids or aqueous sodium hydroxide. They are somewhat sparingly soluble in cold alcohol, and sparingly soluble in other usual organic solvents when cold (ethyl acetate, acetone, ether, chloroform, or benzene).

6-*Hydroxy-2-methyltetrahydro*iso*quinoline*,



This base separates from ethyl acetate in prismatic needles, which melt at 182—183° (corr.):

0·1486 gave 0·4000 CO_2 and 0·1060 H_2O. C=73·4; H=8·0.

$C_{10}H_{13}ON$ requires C=73·6; H=8·0 per cent.

*6-Benzoyloxy-2-methyltetrahydro*iso*quinoline* crystallises from dilute alcohol in clear, colourless prisms, which melt at 91—92° (corr.), and contain half a molecular proportion of water of crystallisation, which is not lost in a vacuum over sulphuric acid, but escapes at 100°.

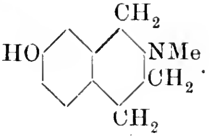
It is insoluble in water, somewhat sparingly soluble in cold alcohol, but readily so in hot alcohol:

0·1576 * gave 0·4252 CO_2 and 0·0930 H_2O. C=73·5; H=6·6.

0·1566 * lost 0·0052 at 100°. H_2O=3·3.

$C_{17}H_{17}O_2N,\frac{1}{2}H_2O$ requires C=73·9; H=6·6; H_2O=3·3 per cent.

*7-Hydroxy-2-methyltetrahydro*iso*quinoline*,



This base was obtained both by hydrolysis of its benzoyl derivative separated from the mixed phenolic bases above described, and also by the reduction of 7-hydroxy*iso*quinoline methiodide. In each case it crystallises from acetone in beautiful, refracting prisms, which melt at 171—172° (corr.), together with a mixture of the base from both sources:

0·1510 gave 0·4070 CO_2 and 0·1106 H_2O. C=73·4; H=8·2.

$C_{10}H_{13}ON$ requires C=73·6; H=8·0 per cent.

*7-Benzoyloxy-2-methyltetrahydro*iso*quinoline* crystallises from alcohol in clusters of thin, clear, nearly rectangular plates, which melt at 97—98° (corr.). It is insoluble in water, somewhat sparingly soluble in cold alcohol, but readily so in hot alcohol:

0·1502 gave 0·4180 CO_2 and 0·0880 H_2O. C=75·9; H=6·5.

$C_{17}H_{17}O_2N$ requires C=76·4; H=6·4 per cent.

The *hydrobromide* crystallises from water in clusters of jagged plates or needles, which melt at 222—224° (corr.). It is easily soluble in hot, but sparingly so in cold water, and is anhydrous:

0·1408 gave 0·3030 CO_2 and 0·0676 H_2O. C=58·7; H=5·4.

0·1762 „ 6·2 c.c. N_2 at 21° and 764 mm. N=4·1.

0·2345 „ 0·1262 AgBr. Br=22·9.

$C_{17}H_{17}O_2N,HBr$ requires C=58·6; H=5·2; N=4·0; Br=23·0 per cent.

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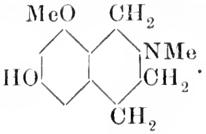
* Air-dried.

*6-Hydroxy-8-methoxy-2-methyltetrahydro*iso*quinoline*,



This base crystallises from ethyl acetate in clusters of flat needles, which melt at 202—203° (corr.):

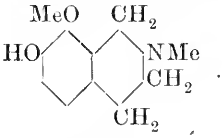
0·1400 gave 0·3496 CO_2 and 0·0962 H_2O. C=68·1; H=7·7.
$C_{11}H_{15}O_2N$ requires C=68·4; H=7·8 per cent.

The *hydriodide* separates from water in clear plates, which melt at 224—225° (corr.). It is readily soluble in hot, but sparingly so in cold water:

0·1540 gave 0·2328 CO_2 and 0·0730 H_2O. C=41·2; H=5·3.
0·1575 ,, 0·1147 AgI. I=39·4.
$C_{11}H_{15}O_2N,HI$ requires C=41·1; H=5·0; I=39·5 per cent.

A fraction of a gram of this base when heated to 160° with a few c.c. of concentrated hydrochloric acid for one hour gave, on subsequent evaporation, a brown syrup, of which the aqueous solution gave no coloration with ferric chloride.

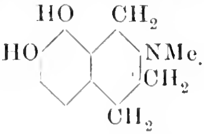
*7-Hydroxy-8-methoxy-2-methyltetrahydro*iso*quinoline*,



This base crystallises from alcohol in clear, thin, diamond-shaped plates, which melt at 163—164° (corr.):

0·1400 gave 0·3512 CO_2 and 0·0986 H_2O. C=68·4; H=7·9.
$C_{11}H_{15}O_2N$ requires C=68·4; H=7·8 per cent.

A small amount of this base when heated to 150° with a large excess of concentrated hydrochloric acid for half an hour gave on evaporation to dryness a crystalline residue of 7:8-*dihydroxy-2-methyltetrahydro*iso*quinoline hydrochloride*,



This salt crystallises from water in prismatic needles, which melt and decompose at 280° (corr.). It is somewhat sparingly soluble in cold water. Its aqueous solution gives with ferric chloride a green coloration, which becomes red on the addition of sodium carbonate. When treated with aqueous sodium hydroxide, aqueous solutions of this salt readily blacken owing to oxidation:

0·1518 * gave 0·3116 CO_2 and 0·0922 H_2O. C = 56·0; H = 6·8.
$C_{10}H_{13}O_2N,HCl$ requires C = 55·7; H = 6·5 per cent.

*7-Benzoyloxy-8-methoxy-2-methyltetrahydro*iso*quinoline* crystallises from alcohol in glistening plates, which melt at 121—122° (corr.). It is insoluble in water, but sparingly soluble in cold alcohol:

0·1565 gave 0·4160 CO_2 and 0·0896 H_2O. C = 72·5; H = 6·4.
$C_{18}H_{19}O_3N$ requires C = 72·7; H = 6·4 per cent.

The *hydrobromide* crystallised from water in glistening leaflets, which melt and decompose at 264° (corr.), after sintering a few degrees earlier. It is rather sparingly soluble in hot, and very sparingly so in cold, water:

0·1784 gave 0·3761 CO_2 and 0·0901 H_2O. C = 57·5; H = 5·6.
0·2919 „ 0·1436 AgBr. Br = 20·9.
$C_{18}H_{19}O_3N,HBr$ requires C = 57·1; H = 5·3; Br = 21·1 per cent.

Reduction of Hydrohydrastinine.

Five grams of hydrohydrastinine were reduced by means of 25 grams of sodium and sufficient anhydrous fusel oil, and the reaction product worked up as in the case of hydrocotarnine. 2·75 Grams of unchanged hydrohydrastinine were recovered, together with 1·65 grams of syrupy phenolic bases. The latter were dissolved in a little ethyl acetate, and deposited 0·3 gram of crude 6-hydroxy-2-methyltetrahydro*iso*quinoline, melting at 170°, which was purified by crystallisation from ethyl acetate. The ethyl acetate mother liquor was evaporated to dryness, and benzoylated as previously described, when 0·6 gram of 7-benzoyloxy-2-methyltetrahydro*iso*quinoline hydrobromide, melting at 220°, was obtained.

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* Dried at 100°.

CLXXIII.—*Nitrites of Primary, Secondary, and Tertiary Bases.*[*]

By Pañchānan Neogi, M.A.

Coniinium Nitrite, $C_8H_{17}N,HNO_2$.

A solution of coniinium nitrite was prepared in the usual manner. The solution was neutral, and liberated iodine copiously from an acidified solution of potassium iodide. The solution could be concentrated to a small bulk on the water-bath, and when kept in a vacuum desiccator over concentrated sulphuric acid gave long, colourless, fibrous crystals, which were found on analysis to be pure coniinium nitrite. The crystals were deliquescent and very soluble in water or alcohol, and almost insoluble in ether:

0·0994 gave 13·2 c.c. N_2 at 19° and 750 mm. (made up to 10 c.c. with water, of which 1 c.c. = 3·2 c.c. N_2). N("nitritic") = 7·45.

$C_8H_{17}N,HNO_2$ requires N("nitritic") = 8·0 per cent.

The nitrite when subjected to steam distillation under diminished pressure was found to distil in very appreciable quantities.

Sublimation and Decomposition of Coniinium Nitrite.

The crystals were heated in the vacuum of the Töpler pump in a long, hard glass tube immersed in a sulphuric acid bath. The crystals began to sublime at 55°, and the greater part sublimed in beautiful clusters of fibrous crystals when the temperature was maintained between 70° and 80°. When the temperature was raised to 90°, the few crystals remaining at the bottom of the tube melted to a reddish-yellow liquid. As the temperature was raised to 110° the whole quantity sublimed. No gas collected in the Crum nitrometer. The liquid again solidified when the bath was taken away.

The salt was next heated under ordinary pressure. The temperature was rapidly raised to 100°, and the crystals, which melted at about 84—86°, gave a reddish-yellow liquid, which did not solidify on cooling. The temperature was finally raised to 120° in order to complete the decomposition. The resulting liquid was sparingly soluble in water, but readily so in alcohol or ether. It boiled under the ordinary pressure at 150—155°, and readily gave the

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[*] For abstract, see Proc., 1912, **28**, 53.

nitroso-reaction. The liquid therefore was nitrosoconiine. The decomposition is represented by the following equation:

$$C_8H_{17}N,HNO_2 = C_8H_{16}N\cdot NO + H_2O.$$

Preparation of Coniinium Nitrite by the Interaction of Coniinium Hydrochloride and Alkali Nitrites.

It has already been shown (Proc., 1911, **27**, 242) that benzylammonium nitrite, piperidinium nitrite, and triethylammonium nitrite can be prepared by distilling and subliming in a vacuum a concentrated solution of the hydrochlorides of the bases and alkali nitrites. Coniinium nitrite has also been obtained in fairly large quantities in a slightly modified manner.

I. At first attempts were made to prepare the compound by sublimation in a vacuum. Half a gram of the hydrochloride purified by crystallisation from alcohol (Found, Cl = 21·2. $C_8H_{17}N\cdot HCl$ requires Cl = 21·7) was mixed with molecular quantities of sodium or potassium nitrite, and dissolved in a small quantity of water. The liquid was evaporated to dryness at 40° to 50° in the vacuum of a Töpler pump. No gas was evolved. The temperature was raised to 90°, but sublimation was observed only to a very slight extent. The distillate, however, liberated iodine freely from an acidified solution of potassium iodide, and evolved the vapours of coniine when heated with sodium hydroxide solution. The liquid when kept in a vacuum desiccator gave a small quantity of coniinium nitrite.

II. A much better yield, however, of the nitrite was obtained by a modified process, namely, vacuum distillation in steam. The operation was conducted in two ways: (1) distilling the solution in a current of steam whilst a vacuum was maintained, and (2) repeatedly distilling in a vacuum the mixture with fresh quantities of water. The first of these two processes has the advantage of being continuous, but the bumping is very severe. The second process gives the better yield. The best results were obtained in the following manner. The solution of the mixture was placed in a distilling flask (1000 c.c.) connected with a long condenser and receiver, which was in turn connected with a Geryk pump and manometer. The solution was diluted with water, so as to fill not more than one-third of the flask, which was held in a very slanting position in order that the spirting liquid might not enter the neck of the flask. The flask was immersed in a beaker containing water, which served as a bath. When the maximum reduction of pressure was obtained, the temperature of the bath was rapidly raised to 70°, and maintained between 70° and 80° until the liquid was evaporated to dryness. The flask was cooled, and the receiver detached. More water was added to the distilling flask, and a second distillate obtained. In this way four or five distillates were collected, which contained appreciable quantities of the nitrite. The total volume of the distillates was between 400 and 500 c.c. The nitrite was wholly free from chlorides. The solution was then concentrated to a small bulk on the water-bath, and finally crystallised in a vacuum desiccator over concentrated sulphuric acid, when long, fibrous crystals of coniinium nitrite were obtained.

The crystals were analysed as usual by the "urea" and Crum-Frankland method. In this way from 0·5 gram of the hydrochloride more than 0·1 gram of the pure nitrite was obtained, although a portion of it was lost with the steam during the concentration of the distillate on the water-bath. The crystals sublimed almost entirely when heated in a vacuum to 70—80°. (Found, N("nitritic") = 7·6. Calc., N("nitritic") = 8·0 per cent.)

It has already been shown that coniinium nitrite when heated at ordinary pressure decomposes, yielding the corresponding nitroso-compound, so that the formation of the nitroso-compound by the interaction of nitrous acid on coniine is simply the end-product of the reaction, the intermediate compound being a nitrite. The actual isolation of ammonium nitrite (Neogi and Adhicāri, Trans., 1911, **99**, 116), benzylammonium nitrite, piperidinium nitrite, and triethylammonium nitrite (Neogi, Proc., 1911, **27**, 242) from a mixture of the hydrochlorides of the bases and sodium or potassium nitrite, as well as the fact that these nitrites decompose, yielding the end-products of the reactions, definitely show that a nitrite is the intermediate compound in the action of nitrous acid on the primary, secondary, and tertiary amines.

These observations, of course, do not apply to those aromatic amines, such as aniline, which yield diazo-compounds.

The details of the experiments with benzylammonium nitrite, piperidinium nitrite, triethylammonium nitrite, and other amine nitrites will be described in separate communications.

Coniine Methonitrite, $C_8H_{17}N,CH_3\cdot NO_2$.

A solution of coniine methonitrite was obtained in the usual manner. The liquid was neutral, and could be concentrated to a small bulk on the water-bath. When kept in a vacuum desiccator over concentrated sulphuric acid, it gave a viscous, reddish-yellow liquid, which on analysis was found to be the methonitrite:

0·3340 gave 42·0 c.c. N_2 (made up to 10 c.c. with water, of which 1 c.c. = 4·2 c.c. N_2) at 23° and 755 mm. N("nitritic") = 7·2.
$C_8H_{17}N,CH_3{\cdot}NO_2$ requires N("nitritic") = 7·4 per cent.

The liquid was soluble in water or alcohol, but insoluble in ether.

Piperidine Ethonitrite, $C_5H_{11}N,C_2H_5{\cdot}NO_2$.

The solution of the nitrite was prepared in the usual manner. It was neutral, and could be concentrated on the water-bath to a small bulk. On evaporating the solution to dryness in a vacuum desiccator over sulphuric acid, the nitrite was obtained in colourless plates. When analysing the substance hy the "urea" and Crum-Frankland methods, it was found that the volume of nitric oxide obtained by the Crum-Frankland method was not constant. In one case 1 c.c. of the solution gave 6·2 c.c. and 10·4 c.c. gas in two consecutive experiments, whilst the volume of nitrogen by the "urea" method was 2·8 c.c. only. Evidently concentrated sulphuric acid decomposes the substance completely instead of liberating nitric oxide only:

0·1630 gave 28·0 c.c. N_2 (made up to 10 c.c. with water, of which 1 c.c. = 2·8 c.c. N_2) at 30° and 755 mm. N("nitritic") = 9·2.
$C_5NH_{11},C_2H_5{\cdot}NO_2$ requires N("nitritic") = 8·75 per cent.

The crystals were deliquescent, very soluble in water or alcohol, but not in ether.

Pyridine Ethonitrite, $C_5H_5N,C_2H_5{\cdot}NO_2$.

The solution of the nitrite was neutral, and could be concentrated to a small bulk on the water-bath. When kept in a vacuum desiccator over concentrated sulphuric acid, the nitrite was obtained as an almost colourless liquid, slightly tinged yellow. The liquid was soluble in water or alcohol, and insoluble in ether:

0·3990 gave 62·0 c.c. N_2 (made up to 10 c.c. with water, of which 1 c.c. = 6·2 c.c. N_2) at 19° and 755 mm. N("nitritic") = 8·8.
$C_5H_5N,C_2H_5{\cdot}NO_2$ requires N("nitritic") = 9·09 per cent.

The action of heat on these compounds is being studied, and the examination of other nitrites of this series is being continued.

CLXXIV.—*The Essential Oil of the Leaves of* Atherosperma moschatum (*"Australian Sassafras"*).

By MARGARET E. SCOTT.

Atherosperma moschatum, Labill. (Nat. Ord. *Monimiaceae*), known as "Australian Sassafras," although having no connexion with the *Sassafras officinale* of the British Pharmacopœia, grows luxuriantly in gullies among ranges, such as those around Healesville and Warburton in Victoria. The leaves and bark of the tree have some medicinal repute locally, and oils were distilled from them many years ago by Bosisto, but they were not chemically examined.

The leaves employed for the present investigation were obtained from Warburton, through the kindness of Mr. Dowey, of the Forestry Department, and from Sassafras, and were distilled within two or three days after picking. The yield of oil varied, in different samples, from 1·7 to 2·65 per cent. During the steam distillation it was observed that the first portion of oil (about 30 per cent. of the whole) was lighter than water, whilst that which subsequently passed over was heavier than water and sank to the bottom of the vessel.

About 3 litres of crude oil were obtained, which, after drying over calcium chloride, had a pale yellow colour and the characteristic sassafras odour. Its physical constants were as follows: D 1·027; $[\alpha]_D + 7·5°$; n_D 1·5211.

The oil was first distilled under diminished pressure (100 mm.), and was thus divided into sixteen fractions, ranging in boiling point from 99° to 183°. The optical rotation of fractions 1—9 ranged from +61·7 to +1·7°, the remaining seven fractions being optically inactive. The density of the fractions varied from 0·881 in No. 1 to 1·034 in No. 16, whilst the refractive index of the same fractions was 1·4687 and 1·5322 respectively.

The above-mentioned sixteen fractions were subsequently subjected to repeated fractional distillation at the ordinary pressure, with the use of the rod-and-disk dephlegmator described by Young.

Identification of Pinene, $C_{10}H_{16}$.

A fraction boiling at 157—158°, which was a colourless liquid, was analysed. (Found, C = 87·99; H = 11·65. $C_{10}H_{16}$ requires C = 88·23; H = 11·77 per cent.)

The identity of this fraction with pinene was determined by the formation of a crystalline hydrochloride (m. p. 130°) and the nitrosochloride, which melted sharply at 103°. The amount of material was insufficient for determining its optical rotation.

Identification of Camphor, $C_{10}H_{16}O$.

Five successive fractions of the oil yielded on distillation a solid substance, which, when collected and purified from adhering oil, was white and crystalline, possessed the characteristic odour of camphor, and melted at 174·5—176°. (Found, $C=78·87$; $H=10·58$. $C_{10}H_{16}O$ requires $C=78·94$; $H=10·52$ per cent.)

A determination of the optical rotatory power of the substance proved it to be *d*-camphor, for a 10 per cent. solution in alcohol (D 0·820) gave $[\alpha]_D +40·66°$.

Identification of Eugenol Methyl Ether, $C_{11}H_{14}O_2$.

The largest portion of the oil, after repeated fractionation, was a pale yellow liquid, which distilled at 251·7°/755 mm. (Found, $C=73·63$; $H=7·88$. $C_{11}H_{14}O_2$ requires $C=74·15$; $H=7·86$ per cent.)

The further identification of this fraction with eugenol methyl ether was effected by the formation of a bromo-derivative, which, after crystallisation from alcohol, melted at about 75°.

Identification of Safrole, $C_{10}H_{10}O_2$.

The portions of the oil possessing the highest boiling point were found to be a mixture of eugenol methyl ether with another compound, the separation of which was effected by repeated fractional distillation. A nearly colourless liquid was thus obtained, which boiled at 233°, and had the characteristic odour of safrole. (Found, $C=74·47$; $H=6·03$. $C_{10}H_{10}O_2$ requires $C=74·07$; $H=6·17$ per cent.)

On exposing the liquid to the temperature of boiling liquid ammonia, it congealed, forming white, silky needles, which melted at a temperature of 8—12°. The identity of this substance with safrole was thus established.

From the results of this investigation it may be concluded that the essential oil of *Atherosperma moschatum*, Labill., contains the following compounds in approximately the proportions indicated: eugenol methyl ether, 50—60 per cent.; pinene, 15—20 per cent.; camphor, 15—20 per cent.; and safrole, 5—10 per cent.

The author desires to thank Professor Orme Masson, Professor B. D. Steele, and Dr. Heber Green for kind encouragement and advice during the course of this work.

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CLXXV.—*Alkaline Cupri-compounds.*

By Spencer Umfreville Pickering, M.A., F.R.S.

From a solution of copper racemate in sodium hydroxide, left with a layer of alcohol above it, Werther (*J. pr. Chem.*, 1844, **32**, 393) obtained, in two different crystalline forms, a substance represented as $C_4H_4O_6Na_2,CuO,4H_2O$. Bullnheimer and Seitz (*Ber.*, 1899, **32**, 2347; 1900, **33**, 817), by dissolving copper tartrate or racemate in alkalis, or by digesting potassium or sodium racemate with copper hydroxide and alkalis, concentrating the resulting liquids with alcohol, and evaporating over sodium hydroxide, obtained various compounds which they represented as belonging to two series, one derived from an alkali metal tartrate by the substitution of Cu for 2H in the $(CH\cdot OH)_2$-group, and the other from a combination of such a molecule with a second similar molecule having an alkali metal in the place of the copper:

(1) $(CHO)_2Cu(CO_2M')_2$, and

(2) $(CHO)_2Cu(CO_2M')_2,(CHOM')_2(CO_2M')_2$.

It is impossible to reconcile the first of these formulæ with the fact that the substances were strongly alkaline, and it will be shown, as, indeed, is apparent from Bullnheimer and Seitz's own results in some cases,* that these formulæ fall short of the minimum molecular weights of the substances by quantities equivalent to the elements of one or more molecules of water.

The compounds described below, including some which are not alkaline, may be represented empirically as molecules of copper tartrate or racemate (both written RCu), or of the double salts, $R_2CuM'_2$ (M'=K, Na or Li), united with CuO, M'_2O or $M'OH$: and they may be designated by the proportion of copper to alkali metal present. Twenty-four substances, representing ten different types of compounds, have been obtained, and, with the exception of four salts representing one of these types, they are all crystalline. Especially with those compounds in which the proportion of alkali is large, they resemble the alkaline cupricitrate (Luff's salt; Trans., 1910, **97**, 1842), and are strongly differentiated from the cupritartrates previously described, which contain CuO in the alcoholic hydroxyl portion of the molecule (Trans., 1911, **99**, 169): they are not (except in one case) precipitated as emulsions, nor form scaly substances on drying; they do not reabsorb water with decrepita-

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* Details as to the preparation and behaviour of the compounds are deficient in several cases, and further information has not been procurable, as the work was done by Seitz, whose whereabouts are at present unknown.

tion, and, on decomposition by heat, they do not scatter, or give off copper smoke.

The analytical results are summarised in the following table. The number of different preparations obtained and analysed are given in col. I; the percentages of copper and alkali metal in cols. III and IV refer to the anhydrous salt. The atomic ratios (cols. V—VII) include that of the water retained at 100°: in some cases (those given in brackets) this did not show a satisfactory constancy with different specimens. The temperatures of dehydration are given in col. II: these require explanation. When the substances are heated to incipient decomposition, cuprous oxide is formed: this, if present in moderate proportion, makes a solution of the salt appear green and opaque, but the blue colour reasserts itself when the cuprous oxide is allowed to settle. If the amount of decomposition is very minute, the substance dissolves to form a solution which is green or greenish, but perfectly clear, and which, after an hour or so, becomes quite blue: presumably the green tinge in this case, also, is due to the presence of cuprous oxide in very minute quantities, which eventually re-enters into combination. The appearance of this green colour on dissolving the salt was, therefore, used to determine its decomposition temperature, and that adopted for desiccation was 5° or 10° lower. As the decomposition temperature varied slightly according to the conduct of the heating, it was determined separately in each case, two portions being heated simultaneously, one to serve for the analysis, the other for ascertaining when decomposition started. In nearly every case the loss in weight occurring between the temperature of desiccation and that at which decomposition was conspicuous (the sample becoming yellow at the bottom) was very small, and considerably less than the xH_2O which would be necessary to render formulæ with Cu substituted for 2H acceptable. The formulæ assigned to these compounds will be discussed later on.

The water contained in the unheated substances was generally not determinable with any certainty, for they absorb carbon dioxide gradually when moist, and must, therefore, be dried by exposure over alkalis, entailing the possibility of some dehydration.

Rough determinations of the solubility are entered in col. IX of the table. These refer to a temperature of 10°, and are expressed as grams of copper in 100 c.c. of solution.

Copper Racemate and Strong Solutions of Alkalis.

The following reactions will be alluded to when describing the salts:

(1) Copper racemate and sodium hydroxide (a 20 per cent.

solution) in the proportions RCu : 2 to 12NaOH. The racemate dissolves completely in all cases: with 2NaOH the liquid becomes nearly solid in two or three minutes through the crystallisation of the 1 : 2 compound: with larger portions of alkali (4NaOH) the crystallisation does not begin until after ten minutes, the crystals

Analytical Results.

		Per cent. on anhydrous		Ratio.				
Number of samples. I.	Temperature of dehydration. II.	Cu. III.	M′. IV.	Cu. V.	M′. VI.	H_2O at 100°. VII.	Molecular weight.* VIII.	Solubility grams of Cu in 100 c.c. IX.
Potassium cupriracemate, 4 : 3. $(R_2CuK_2)_3,5CuO$.								
9	130—140°	29·80	14·20	4	3·10	(2·23)	849·4	2·2
Calc.	—	*29·72*	*13·71*	*4*	*3·00*	—	*855·6*	—
Sodium cupriracemate, 4 : 3. $(R_2CuNa_2)_3,5CuO$.								
6	150—160°	31·75	8·74	4	3·04	3·55	795·2	1·5
Calc.	—	*31·50*	*8·55*	*4*	*3·00*	—	*807·3*	—
Lithium cupriracemate, 4 : 3. $(R_2CuLi_2)_3,5CuO$.								
3	145—150°	33·16	2·77	4	3·12	3·52	764·1	(15·0)
Calc.	—	*33·48*	*2·78*	*4*	*3·00*	—	*759·5*	—
Potassium cupritartrate, 4 : 3. $(R_2CuK_2)_3,5CuO$.								
2	100°	29·58	13·51	4	2·99	0·00	863·9	18·0
Calc.	—	*29·72*	*13·71*	*4*	*3·00*	—	*855·6*	—
Sodium cupritartrate, 4 : 3. $(R_2CuNa_2)_3,5CuO$.								
2	130°	31·92	8·70	4	3·01	(2·95)	794·9	14·0
Calc.	—	*31·50*	*8·55*	*4*	*3·00*	—	*807·3*	—
Potassium cupriracemate, 1 : 1. $R_2CuK_2,RCu,2CuO,2KOH$.								
3	130°	27·04	16·75	1	1·01	0·38	927·2	—
Calc.	—	*27·62*	*16·99*	*1*	*1·00*	—	*920·8*	—
Sodium cupriracemate, 1 : 1. $R_2CuNa_2,RCu,2CuO,2NaOH$.								
3	130—150°	28·79	10·92	1	1·11 †	0·50	860·8	—
Calc.	—	*29·69*	*10·74*	*1*	*1·00*	—	*856·4*	—
Sodium cupritartrate, 1 : 1. $R_2CuNa_2,RCu,2CuO,2NaOH$.								
1	145°	27·27	11·78	1	1·19	0·45	856·8	—
Calc.	—	*29·69*	*10·74*	*1*	*1·00*	—	*856·4*	—
Lithium cupritartrate, 1 : 1. $R_2CuLi_2,RCu,2CuO,2LiOH$.								
1	120°	30·55	3·72	1	1·12	0·28	594·0	—
Calc.	—	*32·09*	*3·55*	*1*	*1·00*	—	*592·4*	—
Potassium cupriracemate, 1 : 2. RCu,K_2O.								
5	130°	21·24	25·71	1	1·97	0·54	301·8	13·4
Calc.	—	*20·79*	*25·51*	*1*	*2·00*	—	*305·8*	—

* Mean values from the Cu and M′ percentages given for the minimum molecular weights with the ratios indicated.

† The most satisfactory sample gave 1 : 1·01.

Analytical Results (continued).

Number of samples.	Temperature of dehydration.	Per cent on anhydrous		Ratio.			Molecular weight.*	Solubility, grams of Cu in 100 c.c.
I.	II.	Cu. III.	M′. IV.	Cu. V.	M′. VI.	H_2O at 100°. VII.	VIII.	IX.
Sodium cupriracemate, 1 : 2. RCu,Na_2O.								
4	115—120°	23·21	17·14	1	2·03	0·57	271·1	1·79
Calc.	—	*23·24*	*16·81*	*1*	*2·00*	—	*273·6*	—
Potassium cupriracemate, 2 : 5. $R_3Cu_2K_2,K_2O,KHO$.								
2	100°	15·76	23·69	2	4·89	0·00	812·9	2·82
Calc.	—	*15·90*	*24·45*	*2*	*5·00*	—	*799·7*	—
Sodium cupriracemate, 2 : 5. $R_2CuNa_2,Na_2O,CuO,NaOH$.								
4	115—120°	20·37	19·03	2	5·13	2·06	612·4	1·36
Calc.	—	*21·65*	*19·58*	*2*	*5·00*	—	*587·2*	—
Sodium cupriracemate, 1 : 3. $RCu,Na_2O,NaOH$.								
2	125°	19·94	21·10	1	2·93	1·20	322·9	1·20
Calc.	—	*20·27*	*22·00*	*1*	*3·00*	—	*313·6*	—
Potassium cupriracemate, 1 : 4. R_2CuK_2,K_2O.								
1	130°	12·15	29·69	1	3·97	2·41	525·0	1·81
Calc.	—	*11·95*	*29·40*	*1*	*4·00*	—	*532·0*	—
Sodium cupriracemate, 1 : 4. $RCu,2Na_2O$.								
6	115—130°	14·78	22·35	1	4·11	(1·80)	420·9	0·85
Calc.	—	*14·59*	*21·12*	*1*	*4·00*	—	*435·6*	—
Potassium cupriracemate, 1 : 5. R_2CuK_2,K_2O,KOH.								
1	120°	10·23	33·50	1	5·20	2·89	602·5	—
Calc.	—	*10·81*	*33·40*	*1*	*5·00*	—	*588·1*	—
Sodium cupriracemate, 1 : 5. $R_2CuNa_2,Na_2O,NaOH$.								
1	100°	12·61	22·46	1	4·92	0·00	508·1	0·88
Calc.	—	*12·22*	*22·65*	*1*	*5·00*	—	*507·6*	—
Potassium cupriracemate, 1 : 6. $R_2CuK_2,2K_2O$.								
1	115°	9·92	36·25	1	5·99	0·00	641·4	6·0
Calc.	—	*10·15*	*37·46*	*1*	*6·00*	—	*626·2*	—
Sodium cupriracemate, 1 : 6. $R_2CuNa_2,2Na_2O$.								
5	125—135°	11·91	25·30	1	5·87	3·00	534·6	1·19
Calc.	—	*12·00*	*26·06*	*1*	*6·00*	—	*529·6*	—
Potassium cupritartrate, 1 : 6. $R_2CuK_2,2K_2O$.								
1	—	—	—	1	5·93	—	—	—
Calc.	—	—	—	*1*	*6·00*	—	—	—
Sodium cupritartrate, 1 : 6. $(R_2CuNa_2),2Na_2O$.								
3	100°	11·81	25·33	1	5·90	0·00	541·6	6·5
Calc.	—	*12·00*	*26·06*	*1*	*6·00*	—	*529·6*	—
Potassium and sodium cupritartrate, 1 : 2 + 4. $R_2CuK_2,4NaOH$.								
1	100°	10·78	13·00 14·72	1	1·96 3·77	0·00	605·4	—
Calc.	—	*10·63*	*13·08* *15·39*	*1*	*2·00* *4·00*	—	*597·8*	—

separating being quite different from those of the 1:2 compound, and consisting of a 1:3 compound. By inoculating the mother liquor with some of the 1:2 substance a crystallisation of this salt may be obtained in the same liquid as that containing the crystals of the 1:3 substance. With still larger proportions of alkali, 6 to 12 NaOH, crystallisation occurs less readily, and the compound separating shows the ratio 1:4.

In similar experiments with potassium hydroxide, crystallisation does not occur spontaneously, but, on the addition of alcohol, the liquid becomes concentrated, and eventually solidifies to a mass of crystals, which in all cases consists of the 1:2 compound. Probably compounds containing more potassium are formed initially, where excess of alkali is used, and are reduced to the 1:2 compound by the alcohol.

(2) With copper racemate, racemic acid, and sodium hydroxide in the proportions of $RCu:RH_2:3$ to 6NaOH (the acid being first dissolved in the alkali, and the copper racemate added to the mixture), a clear solution is obtained in all cases: with 3NaOH taken, the liquid becomes almost solid in a few minutes, through the deposition of a questionably crystalline precipitate of the 1:1 compound. With 4NaOH definite crystallisation of the 1:2 compound occurs after twenty minutes, and with larger proportions of alkali this become mixed with the 1:6 compound, which is the sole product when the alkali taken amounts to 6NaOH.

Similar results as regards the formation of a 1:1 compound were obtained on using potassium hydroxide, but with the larger proportions of alkali no crystallisation occurred, and the only compound obtained with certainty on evaporation of the resulting liquids in a vacuum was the 1:5 compound. In many cases the product was contaminated with crystals of potassium racemate.

4:3 *Compounds*, $(R_2CuK_2)_3,5CuO$.

It is remarkable that these should not have been previously obtained.

Copper racemate dissolves easily in 2 to 10 per cent. solutions of alkaline hydroxides: after about ten minutes in the cases of the sodium and potassium salts, a copious crystallisation begins, proceeding for about two days, until little of the copper is left in the solution. The crystals are small, especially in the case of the sodium compound, and consist of tetrahedra of a rather pale blue colour and neutral reaction. All fractions have the same composition, unless visibly contaminated with cuprous oxide, which occurs sometimes. With alkali sufficiently dilute to obviate crystallisation, the amount of copper racemate dissolving is 8RCu for every

10M′OH, indicating the entire conversion of the reagents into the 4:3 compound.

Although fairly soluble, the sodium salt dissolves with remarkable slowness in water, the liquid remaining cloudy for some hours.

The potassium salt is also obtained when the 1:1 compound, described below, is dissolved in a little water, the clear solution becoming opaque after a time, through the separation of the 4:3 compound in minute, glistening crystals. The sodium salt is not obtainable in this way, the precipitate forming in parallel circumstances not being crystalline nor of definite composition.

The 4:3 lithium compound does not crystallise spontaneously from a solution of copper racemate in lithium hydroxide, but, on the addition of alcohol insufficient to cause cloudiness, it separates gradually in microscopic crystals.

The sodium and lithium salts both retain $7H_2O$ at 100° (on a formula with 8Cu in the molecule): that retained by the potassium salt varied from 3 to 7 H_2O.

A solution of copper tartrate in sodium hydroxide behaves in the same way as one of the racemate in lithium hydroxide, and nearly the whole of the copper is thrown out of solution. The crystals form irregular squares, containing, when air-dried, about $24H_2O$, but that retained at 100° varied from 3 to 9.

The potassium cupritartrate is not so easily obtained. Alcohol precipitates as an emulsion the cupritartrate with CuO in the alcoholic hydroxyl group previously described (Trans., 1911, **99**, 169), but if the alcohol is added only to incipient cloudiness, a deposit is formed after some days consisting of large, blue crystals, mixed with other much smaller green ones; the latter can be removed by eleutriation with the mother liquor, when the blue crystals are found to be the 4:3 compound. Two preparations of it were made, but in other cases attempts to obtain it failed.

1:1 *Compounds*, $R_2CuM'_2,RCu,2CuO,2M'OH$.

When copper racemate is dissolved rapidly in weak potassium or sodium hydroxide solution (the alkali in such a case not being entirely neutralised), the solution filtered, and alcohol added before the 4:3 compound has time to separate, a pale blue emulsion is precipitated, which can be dried in a vacuum without liquefying, and then forms a light blue powder, which gives on analysis the ratio 1:1. The corresponding sodium and lithium cupritartrates were obtained in a similar way, although not, apparently, in a very pure condition. The sodium cupriracemate was also obtained, probably, in minute crystals, by the action of concentrated sodium hydroxide on copper racemate, as described under (2) (p. 1618). The corresponding potassium cupriracemate was probably obtained in a similar way, although not satisfactorily pure, the ratio in two cases found being 1:0·87.

All the 1:1 substances differ from the other cupri-compounds here described in that strong solutions of them decompose after a short time, giving a deposit of the 4:3 compound (see p. 1619) or a basic salt. They are alkaline, but this may have been due to the difficulty in washing them completely with alcohol.

1:2 *Cupri-compounds*, RCu,M'_2O.

The potassium cupriracemate was obtained in beautiful crystals by dissolving one molecular proportion of copper racemate in three of potassium hydroxide in the form of 5 per cent. solution, adding a large volume of alcohol until slight cloudiness appeared, and leaving the mixture for some days. Some prismatic crystals formed at the bottom of the vessel, whilst in the liquid there were silky, lavender-blue crystals, some 2 inches long, which, on drying on filter paper, exhibited a beautiful sheen. Both forms of crystals gave the same results on analysis. On being kept for a few days they began to turn green, and eventually decomposed entirely. The corresponding sodium salt was obtained in large, hexagonal crystals by pouring a layer of alcohol on to a solution of copper racemate in excess of sodium hydroxide. It, and also the potassium salt, are formed in the reaction (1) (p. 1615). Both salts contain $5H_2O$ when air-dried, retaining about $0·5H_2O$ at 100°. Both are strongly alkaline.

A potassium cupritartrate with the ratio 1:1·8, which was probably an analogue of the above, was obtained on one occasion: it is not entered in the table.

Werther, as stated, obtained the racemate described as $RNa_2CuO,4H_2O$ (water contents varying in different samples), and Bullnheimer and Seitz, the tartrate RNa_2CuO,H_2O, and the racemates $RLi_2CuO,3H_2O$ and $RK_2CuO,2H_2O$.* It is questionable, however, whether this last compound is identical with that described above, as no mention is made of its peculiar crystalline form, and the water contained in it is different.

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* Apparently by digesting copper hydroxide with the salts of the alkali metals; but attempts to copy this method have failed. They also state that they are obtainable by the process which has yielded nothing but the 4:3 compounds in the present author's hands.

2:5 *Cupri-compounds,* $R_3Cu_2M_2',M_2'O,M'OH$ *and* $R_2CuM_2',M_2'O,CuO,M'OH$.

When a concentrated solution of potassium racemate was digested with excess of copper hydroxide,* the liquid filtered, and shaken up with alcohol, a syrup was obtained, which, after some days' exposure over alkali, began to crystallise. On being stirred, it was converted into a mass of small, blue crystals, which, unlike the other cupri-compounds, appeared opaque. They retained $3{\cdot}5H_2O$ at 100°, and were strongly alkaline.

The sodium salt is obtained by adding alcohol, insufficient to produce cloudiness, to a solution of the 1:6-compound: slender, prismatic crystals with a silky sheen soon begin to separate, and after some hours no copper is left in solution. The crystals are strongly alkaline, but not hygroscopic: they differ in appearance from the potassium analogue, and, as will be mentioned below, must differ from it in constitution.

1:3 *Cupri-compounds,* $RCu,M_2'O,M'OH$.

The sodium cupriracemate was obtained in the reaction (1) (p. 1615). The crystals consist of large, rather violet-blue, irregular squares, hard and gritty, and strongly alkaline.

1:4 *Cupri-compounds,* $RCu,2M_2'O$ *and* $RCuM_2',M_2'O$.

The potassium cupriracemate was obtained by dissolving 1 molecular proportion of copper hydroxide and 2 of racemic acid in 6 of potassium hydroxide solution, concentrating by alcohol, and leaving for twenty-four hours, when it nearly solidified to a mass of hard, light blue, small, rectangular crystals. The sodium cupriracemate was obtained in the reaction (1) (p. 1615), and also by treating the 1:6 compound with alcohol: either a solution of this salt may be mixed with a large volume of alcohol, in which case an emulsion separates, which eventually coalesces and crystallises to the 1:4 substance; or the solid 1:6 compound may be exhausted with alcohol until no more alkali is removed, this occurring when 4Na is left in the molecule. With one preparation the reaction occurred easily on grinding it with cold alcohol; with another, repeated boiling was required.

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* Bullnheimer and Seitz's method of preparing the hydroxide was found to be very satisfactory. Copper sulphate is precipitated with sufficient ammonia to remove all the copper from solution: the basic acid is washed, treated with concentrated alkali, and washed again.

1:5 *Cupri-compounds*, $R_2CuM_2',M_2'O,M'OH$.

The potassium cupriracemate was obtained in the reaction (2) (p. 1618), the substance forming large, dark blue, prismatic crystals.

The sodium salt was obtained in fine, large, octahedral crystals by allowing a solution of the 1:3 compound to remain with a layer of alcohol above it.

1:6 *Cupri-compounds*, $R_2CuM_2',2M_2'O$.

One gram-molecular proportion of copper hydroxide, one of racemic acid, and twelve of potassium hydroxide were warmed with a little water; on cooling or evaporating over alkali, large, deep violet-blue crystals (apparently cubic) were obtained, which agreed well with the above formula. The salt was hygroscopic and soluble. On four other occasions similar crystals were obtained, but showed a deficit of potassium, the ratios varying from 1:5·4 to 1:5·8.

The sodium salt was obtained in the same way, but more easily, owing to its being less soluble. It was also produced in the reaction (2) (p. 1618). It forms large, soft, dark, violet-blue crystals, irregularly hexagonal, scarcely hygroscopic, and only slowly soluble in water. The various preparations all showed some deficit of sodium, the highest ratio being 1:5·92.

The potassium cupritartrate, obtained in the same way as the cupriracemates, was always contaminated with copper oxide, and it was possible to determine only the ratio of Cu:K: this was 1:5·93. Bullnheimer and Seitz, who prepared this salt, apparently found the same difficulty, but do not say how it was overcome, and give a full analysis of the salt, showing a ratio of 1:5·9.

The sodium cupritartrate, prepared by the above method, generally begins to crystallise as soon as the liquid cools. The crystals are hexagonal and large, and contain $12H_2O$. These results agree exactly with those of Bullnheimer and Seitz. These workers also obtained two potassio-sodium cupritartrates with $Cu:(K_2+Na_4)$ and $Cu:(K_3+Na_3)$; the former has been obtained by the present author with a ratio $Cu:K:Na=1:1·96:3·77$, exactly that found by Bullnheimer and Seitz (1:1·97:3·78); it contains, as part of its constitution, the elements of $2H_2O$ more than the corresponding single cupritartrates. All attempts to prepare the K_3+Na_3 compound failed, and it is noticeable that with one of the two preparations of it made by the authors quoted, the ratio found is rather far from that calculated, being Cu : K : Na = 1 : 2·44 : 2·77.

The deficit of alkali metal in many preparations of the 1 : 6 compounds, and the fact that in several cases products were obtained showing ratios intermediate between those of the compounds described, suggested at one time that some of these might be mere mixtures. The marked difference in appearance of the 1 : 2 and 1 : 3 compounds, and the fact that they can be obtained simultaneously at will by inoculating in the same liquid (p. 1618), leaves no doubt as to their separate individuality, but, so far as appearance goes, the 1 : 4 and 1 : 5 products might be mixtures of the 1 : 3 and 1 : 6. The individuality of the 1 : 4 compound was subsequently confirmed by obtaining it by the action of alcohol on the 1 : 6 salt, and doubt, therefore, attaches itself mainly to the 1 : 5 product. The following determinations of the solubilities of the various sodium cupriracemates, however, made simultaneously, show that neither the 1 : 4 nor 1 : 5 compounds can be mixtures of the 1 : 3 and 1 : 6 salts, since their solubility is less than that of either of these latter:

1 : 3.	1 : 4.	1 : 5.	1 : 6.	
1·20	0·85	0·88	1·19	grams Cu in 100 c.c.

Bullnheimer and Seitz refer briefly to a citrate of composition analogous to the 1 : 6 tartrates, to which they assign the formula $C_6H_8O_2Cu(CO_2K)_6,C_3H_4OK(CO_2K)_3$; but various attempts to prepare it were unsuccessful, the sole product obtained being Luff's salt, $C_6H_{10}O_2(CO_2)_6CuK_4,K_2O$. This salt, it was found, is completely precipitated in small crystals from its solution by concentrated potassium hydroxide, even when excess of potassium citrate is present, there being apparently no tendency to form a compound containing more potassium.

Copper Racemate.

Two forms of copper glycerate exist (Trans., 1912, **101**, 177), one the ordinary crystallised salt, the other an amorphous cupri-compound with the empirical formula $(C_3H_5O_3)_2Cu,H_2O$, showing a much greater solubility than the ordinary salt, a lower decomposition temperature, and three times the molecular colour intensity: it is gradually transformed in solution into the ordinary salt. Copper racemate appears to exist in two similar forms.

When to a concentrated solution of sodium racemate (20 per cent. RNa_2) copper sulphate is added (6·5 per cent. $CuSO_4$), the precipitate formed redissolves until the proportions reached are $CuSO_4 : 2RNa_2$, indicating the formation of a soluble double salt,

R_2CuNa_2. With larger proportions, the precipitate becomes permanent, and with $CuSO_4 : RNa_2$ the mixture becomes semi-solid. Increasing the proportion still further, the precipitate redissolves when about $5CuSO_4 : RNa_2$ is reached, and a similar redissolution occurs if water, instead of excess of copper sulphate solution, is added. The proportion of water required indicated that the precipitate is soluble to the extent of about 0·4 gram of copper per 100 c.c., and a similar value was obtained when the precipitate was collected rapidly and shaken with water.

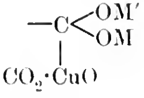
It is amorphous and very bulky, but on being left for half an hour in the liquid, or on being washed on a filter, it changes suddenly to a compact mass of hard, shining, rectangular or hexagonal crystals. If it is collected rapidly, and pressed between paper, it can be rendered apparently almost dry; but it then suddenly liquefies, giving a mixture of the hard crystals and liquid. A determination of the SO_3 in this liquid showed that it was simply mother liquor; hence the precipitate must be identical in composition with the crystallised salt. Its solubility is forty times that of the crystallised salt, and a solution of it obtained in either of the ways mentioned above gradually deposits throughout many days shining crystals of the crystallised salt until the dissolved copper is reduced to about 0·01 per cent. The behaviour of these two forms of copper racemate is analogous, therefore, to that of the two glycerates.

The crystallised racemate was always found to contain $3H_2O$—not $2H_2O$, as generally stated—which it gave up at 100°, decomposing at 190°. On one occasion it was obtained in minute, perfectly spherical particles.

The formation of copper tartrate indicates the probability of changes similar to those observed in the case of the racemate, but much less marked.

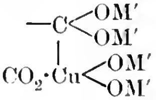
Constitution.

The salts above described supply twenty-two instances in which the empirical formulæ necessitate the copper being present as CuO, and not as Cu displacing hydrogen; the average difference between the found molecular weights and those calculated on the former view is 1·5 per cent. (or algebraically, −0·6), whereas on the latter view it is 7·8 per cent., all the differences being positive. They may be represented as derivatives of the "cupri"-form of copper tartrate or of an alkali-copper tartrate with the group



$$\begin{array}{l}-C\!<\!\begin{matrix}OM'\\OM\end{matrix}\\ \;\;|\\ CO_2\cdot CuO\end{array}$$

or



$$\begin{array}{l}-C\!<\!\begin{matrix}OM'\\OM'\end{matrix}\\ \;\;|\\ CO_2\cdot Cu\!<\!\begin{matrix}OM'\\OM'\end{matrix}\end{array}$$

,

in which M is an atom of hydrogen or alkali metal, or $\frac{1}{2}$Cu. Some of the members would exhibit the same ratio for Cu:M′; this accounts for the sodium and potassium cupriracemates with the ratio 1:4 corresponding with different formulæ.

The four 1:1 compounds, which differ materially in physical properties from the others, can only be represented as derived from a compound molecule of copper tartrate united with a double tartrate: whilst the minimum molecular weight of the 2:5 potassium cupriracemate shows that it must be derived from three racemic nuclei, analogous to one of the cupricitrates and cupricarbonates (Trans., 1910, **97**, 1848; 1911, **99**, 801). Its physical properties indicate that it differs from the majority of the other compounds. The 4:3 salts necessitate on any view the presence of 6 tartaric nuclei, and are easily representable on the same scheme as that applied to the other cases. The great solubility of the 4:3 cupritartrates affords striking evidence that they are not merely basic salts.

HARPENDEN.

CLXXVI.—*The Colour Intensity of Copper Salts.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

ONE of the most characteristic features of cupri-compounds is the depth of their colour. As a standard of comparison, copper sulphate naturally suggested itself: but, as it was sought to extend the measurements to very dilute solutions, it became necessary, in the first instance, to ascertain whether the molecular colour intensity of copper in the sulphate itself varied with dilution. This point has already been partly examined by Sidgwick and Tizard (Trans., 1908, **93**, 187): they found that the colour intensity of copper in the sulphate, chloride, bromide and nitrate—which was the same within a range of 17 per cent., or within 8 per cent. if the nitrate were omitted *—increased on dilution to the extent of 13 per cent. with the sulphate, and 2 to 6 per cent. with the other salts. The standard of comparison used by them was copper sulphate solution containing 1·5 grams of copper per 100 c.c., and, consequently, the range of strength examined was limited, being from 6·4 to 0·9 grams with the sulphate and nitrate, and one-

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* This practical identity had previously been established in a more satisfactory manner by the spectroscopic determinations of Ewan (*Proc. Roy. Soc.*, 1894, **57**, 119). Sidgwick and Tizard give, as a mean, the intensity of copper in the sulphate, chloride and nitrate as 1 : 1·018 : 1·132 ; the present author obtained the values 1 : 1·029 : 0·985.

third of this range with the chloride and bromide. They conjectured that the limiting value for the intensity in still weaker solutions would be less than 1·5, a value, however, which, if approached, would seriously interfere with the use of such weak solutions as standards of comparison for other substances; and, it should be mentioned, the results of Sidgwick and Tizard can hardly be accepted as indicating the existence of a limiting value at all, as they are represented in each case by a straight line. The concordance obtained by these workers in their observations is excellent, and is certainly greater than that attained by the present author, but there seems to have been no attempt to eliminate or estimate errors that must exist in any method which depends on a comparison of the colour of two columns of liquid of different lengths.*

In the present experiments a Stokes' colorimeter was used, with the tubes, *A* and *B*, jacketed in black material. Twelve observations were made with each solution, in six of which the stronger solution was in the tube *A*, in the other six, in *B*; three observations in each case were made with the *A* tube on the right hand side, and three with it on the left. The probable error of the resulting values, determined from the divergence of the individual observations, was ±0·005.

The strongest solution taken was one containing 8 grams of copper per 100 c.c.; in series *A* this was compared with one of one-eighth the strength, adjusting the length of column until the depth of colour appeared the same; the colour of the latter was, in its turn, compared with that of a solution one-eighth weaker again. The results showed a diminution of colour intensity with increased dilution, amounting to 20 per cent. In series *B* the difference in the length of columns compared was reduced to 4:1, and the results showed a diminution of only 7 per cent. In series *C* the difference in the length of columns compared was reduced to 2:1, with the result that the apparent diminution in colour intensity disappeared, there being a difference of 1 per cent. between that of the strongest and weakest solutions, or 3 per cent. between the highest and lowest values obtained. The mean of the values with the nine weaker solutions is 1·003. Any alteration in intensity observed on dilution appears, therefore, to be due to errors introduced by the difference in the lengths of columns compared being too great.

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* The existence of some such error is shown by their results with copper acetate, etc., which, when plotted, indicate a limiting value of 3—4 at infinite dilution; whereas in the present results a reduction to 1—2 has actually been realised in dilute solutions.

TABLE I.

Molecular Colour Intensity of Copper Sulphate in Solutions of Different Strengths.

Grams of copper in 100 c.c.	Relative strengths of the solutions compared.		
	A. 1 and 1/8.	*B.* 1 and 1/4	*C.* 1 and 1/2.
8·0	1·0	1·0	1·0
4·0	—	—	1·004
2·0	—	0·984	1·015
1·0	0·896	—	1·015
0·5	—	0·957	0·996
0·25	—	—	0·995
0·125	0·803	0·937	0·992
0·063	—	—	1·021
0·032	—	—	1·000
0·016	—	—	0·990

In comparing the colour intensity of other salts with copper sulphate, columns of the same, or nearly the same, length were taken where practicable, the strength of the solutions being adjusted so as to obtain equality of coloration. With strong solutions of highly coloured salts (that is, where the colour was deeper than that of a saturated solution of the sulphate) this was impossible, and the results are proportionately less certain, whilst a further element of uncertainty was often introduced by the tint being different from that of the sulphate: in such cases, especially if the tint is violet, the apparent intensity is exaggerated, for on looking across the columns, instead of down through them, much lower values were obtained.* Where these uncertainties existed the values in the following tables are enclosed in brackets, and others, with stronger solutions, have been omitted altogether.

The strength of the solutions examined was halved at each successive observation,† and, to simplify the tables, the values for the same strengths in all cases are entered, these having been deduced from graphs obtained by joining the experimental points by straight lines.

Sidgwick and Tizard examined the formate, acetate and propionate, and found that with all of these the colour intensity diminished with dilution, but that, in the weakest solutions

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* The high values previously given for the colour intensity of copper in the cupricarbonates (Trans., 1909, **95**, 1421, 1423) are, doubtless, erroneous for these reasons.

† The observations were not elaborated to the same extent as when comparing together different solutions of copper sulphate, the unavoidable sources of error preventing exactness.

Table II.

Colour Intensity of Copper in Organic Single and Double Salts.

Grams of copper in 100 c.c.	Single salts.																				Double salts with potassium.				Sulphate and malate.‡
	Formate.	Acetate.	Propionate.	Butyrate.	*iso*Butyrate.	Valerate.	*iso*Valerate.	Pyrotartrate.	Maleate.	Glycerate.*	Malate.	Aconitate.	Tartrate.	Racemate.	Citrate.	Glycollate.	Lactate.†	Benzoate.	Toluate.	Phthalate.	Maleate.	Aconitate.	Pyrotartrate.	Phthalate.	
0·6	—	—	(7·5)	—	—	—	—	—	—	3·4	—	—	—	—	—	—	3·2	—	—	—	—	—	—	—	—
0·4	—	(6·0)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0·3	—	—	6·5	—	—	—	—	—	—	2·8	—	—	—	—	—	—	2·8	—	—	—	—	—	—	20	—
0·2	—	4·6	5·2	5·0	3·2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	17·5	—
0·1	(2·5)	4·0	4·4	4 6	2·9	—	—	—	—	2·5	(6·3)	—	—	—	(8·8)	—	2·8	—	—	—	—	—	—	—	—
0·06	1·8	3·5	3·6	—	—	—	—	—	—	2·4	—	—	—	—	—	2·7	2·4	—	—	—	—	4·0	—	14·5	—
0·04	—	—	3·2	3·8	2·4	—	2·4	—	—	2·3	5·3	—	—	—	—	2·6	—	—	—	—	—	—	—	—	—
0·03	1·6	3·0	3·0	—	—	—	—	—	—	2·3	5·3	—	—	—	7·9	2·6	2·2	—	2·4	6·1	(8·0)	4·0	—	9·8	—
0·02	—	2·7	2·8	3·4	1·8	—	2·0	—	—	2·3	—	—	—	—	—	2·4	—	2·5	—	—	—	—	5·8	—	(10)
0·015	1·4	2·4	2·4	—	—	2·0	—	—	6·0	—	5·5	—	5·4	—	7·1	2·3	2·3	—	1·9	6·2	—	3·8	—	10·2	—
0·01	—	2·2	2·2	2·7	1·7	—	1·6	3·4	5·7	2·2	—	3·3	4·2	3·5	6·7	2·3	2·2	2·2	—	6·1	5·8	—	4·5	9·4	8·5
0·005	1·4	1·9	2·0	2·4	—	1·9	—	3·4	4·9	2·1	5·5	3·3	—	3·5	6·0	2·2	—	2·1	1·4	6·3	5·1	3·9	4·0	8·7	7·2
0·002	—	—	—	—	—	—	—	—	—	—	5·6	—	3·9	3·5	6·2	—	—	—	—	6·0	4·8	3·7	3·2	8·5	6·7
0 001	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	6·3
0·0005	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	4·9	3·3	3·3	—	—

* These values apply to the crystallised salt.

† Satisfactory observations extended to a strength of 2 per cent. Cu, with a colour intensity of 3·1.

‡ Described in Trans., 1912, **101**, 189. Its constitution is doubtful, and it is probably a cupri-compound.

TABLE III.

Colour Intensity of Copper in Cupri-compounds.

Those in Cols. 1—4 are citrates, described in Trans., 1910, **97**, 1841, the second one entered being alkaline (Luff's salt), the others, neutral. Nos. 5—8 are neutral; No. 5, described in Trans., 1911, **99**, 169, and Nos. 6—8 (with CuO in the alcoholic hydroxyl groups) in Trans., 1911, **99**, 169. Nos. 9—25 have been described in this vol., p. 1614; they are all alkaline except the members having a ratio 4Cu : 3M′.

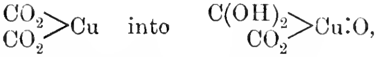
Grams of copper per 100 c.c.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
	Potassium cupri-compounds.								Cupritartrates.					Cupriracemates.											
	Citrate No. 2.	Citrate No. 4.	Citrate No. 6.	Citrate No. 7.	Malate.	Tartrate.	Saccharate.	Mucate.	4Cu : 3K.	4Cu : 3Na.	Cu : 6K.	Cu : 6Na.	Cu : (2K + 4Na).	4Cu : 6K.	4Cu : 6Na.	4Cu : 6Li.	Cu : K.	Cu : Na.	Cu : 2K.	Cu : 2Na.	2Cu : 5K.	2Cu : 5Na.	Cu : 3Na.	Cu : 6K.	Cu : 6Na.
0·3	—	—	—	—	—	—	—	—	—	—	—	—	—	(25)	—	—	—	—	—	—	—	—	—	—	—
0·2	—	—	(20)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0·1	—	—	18·7	—	—	—	—	—	—	(30)	—	—	—	20	—	—	—	—	—	—	—	—	—	—	—
0·06	—	—	—	—	—	—	—	—	—	—	—	—	—	17·3	(29)	—	(22)	(23)	—	—	—	—	—	—	—
0·04	(18·8)	(22)	(18·7)	—	—	(28)	—	—	(24)	21	—	(25)	—	—	—	(22)	—	—	—	—	—	—	—	—	—
0·03	—	—	—	(13)	—	—	—	—	—	—	—	—	—	17·3	18·0	—	19·0	19·5	—	—	—	—	—	—	—
0·02	18·6	21·4	18·7	—	(25)	24	—	—	22	19	—	23	—	16·5	—	21	—	—	—	(21)	—	—	—	—	—
0·015	—	—	—	—	—	—	—	—	—	—	—	—	(25)	—	16·5	—	—	—	(36)	17·0	(12·3)	—	—	—	—
0·01	18·9	19·1	18·7	12·1	20·9	19·3	(37)	(24)	17·8	14·7	(24·0)	23	—	13·7	15·0	15·8	12·0	12·8	18·9	13·7	9·2	(16 2)	(21)	(26)	—
0·005	18·7	19·2	18·8	11·5	16·3	16·2	21·0	(23·0)	15·8	12·3	23·0	23	(17·9)	11·0	13·1	13·3	11·0	11·5	14·0	10·3	7·1	12·8	(11)	(14)	(16·7)
0·002	18·4	19·5	18·8	11·1	12·3	15·1	13·7	(18·5)	12·9	10·5	22·0	21	(12·4)	—	10·4	12·1	10·0	9·6	11·5	9·4	6·7	7·5	(7)	(8)	(10·7)
0·001	18·5	19·5	18·8	—	10·8	—	—	—	12·0	9·6	18·4	19	(12·1)	8·9	8·2	11·2	9·3	8·0	11·3	9·3	—	6·0	—	—	(10·2)
0·0005	—	—	—	—	—	—	—	—	—	—	17·7	19	—	—	—	—	—	—	—	—	—	—	—	—	—
Mean	18·6	19·7	18·7																						

examined, it did not fall below 3·24, 4·36 and 4·15 respectively, showing no tendency to attain a limit of 1—1·5, and indicating, therefore, that such solutions contained no Cu ions. This conclusion appears now to be hardly justified: the weakest solutions examined by them contained as much as 0·15 per cent. of copper (or double that in the case of the formate), and when the investigation is extended to solutions fifteen to thirty times more dilute, as in those entered in table II, the intensity is found, in all the seven cases of the salts of the fatty acids, to show considerable reduction. What the limiting value would be, it is impossible to say, as the fall is still in progress with the weakest solutions examined, but the results are not inconsistent with its being unity.

As regards actual magnitude, the colour intensity in the case of the pyrotartrate, aconitate, glycerate, glycollate, lactate, toluate and benzoate is of the same order as in the case of the fatty acids, whereas in the case of the malate, maleate, tartrate, citrate and phthalate it is conspicuously greater. It is possible that the values in some of these cases might approximate to unity at infinite dilution, but in others there is no appearance of such a limit being reached. No connexion is evident between colour and constitution.

The values with the cupri-compounds, given in table III, are very much higher than those for ordinary copper salts. With the three cupricitrates, first entered, they are practically the same—about 19—and are, moreover, sensibly independent of the strength of solution throughout the range over which accurate comparison is possible. In the other cases the intensity diminishes with dilution, but the maximum from which it falls appears to vary from 18 to 24. The average of all the observations with the strongest solutions of which satisfactory measurements could be made (in five cases none of the measurements were satisfactory) is 19·5; or, omitting three exceptional cases (4, 21 and 22), it is 20·3; but no doubt many of these values are somewhat too high, being affected to some extent by the same source of error which renders observations with still stronger solutions impossible. Hence, 19 may be taken as approximately the colour intensity of the quadrivalent or electronegative copper in these compounds. Nos. 4 and 22 are not really exceptional, for, according to the formulæ suggested for them, some of their copper is in the carboxylic position.

That crystallised double salts of copper do not always exist as such in solution has been demonstrated in the case of the carbonates, since these will not redissolve in the liquids from which they have crystallised; the double citrate will redissolve, but only with an evident change in the nature of the molecule (Trans., 1909, **96**, 1411; 1910, **97**, 1841), this change, it is suggested, being the alteration of the group



$$\begin{matrix}CO_2\\CO_2\end{matrix}\!>\!Cu \quad \text{into} \quad \begin{matrix}C(OH)_2\\CO_2\end{matrix}\!>\!Cu{:}O,$$

the normal salt becoming a cupri-compound. A similar change, partial or complete, is possible in the case of single salts also (Proc., 1910, **26**, 18), and this view, taken together with the fact that copper in such cupri-compounds has a colour intensity much greater than that of dyad or "carboxylic" copper, affords a more satisfactory explanation of the variation in colour intensity of such salts than the theories hitherto advocated.

With inorganic salts the colour intensity has been found to be independent of the electrical conductivity, and it has been concluded, therefore, that the colour intensity of the copper ion, Cu'', must be the same as that of the copper atom in the non-ionised molecule. With organic salts the intensity is greater, and diminishes with the dilution; this has been explained by postulating the presence of complex ions; copper acetate, for instance, ionising into $\overset{+}{AcCu}\,|\,\overset{-}{Ac}$ (Sidgwick and Tizard). Such ionisation, to explain the facts, would have to *decrease* with dilution, and, moreover, is inapplicable in the case of salts of dibasic acids. Its existence seems to be definitely negatived by the results obtained on electrolysing certain cupric salts; for it has been ascertained that the highly coloured ion in such cases is not the cation, but the anion, just as it is in the case of the cupricitrates, cupritartrate and cupricarbonate; thus, with the malate and citrate, of which strong and highly coloured solutions are obtainable, electrolysis in a double vessel connected by a tube containing gelatin reveals a deep blue anion travelling in one direction, and a pale blue cation in the opposite direction. With the other salts giving highly coloured solutions (maleate, tartrate and phthalate), the solubility is too small to yield any dark anion in recognisable quantity,* and this is the case also with the glycerate and lactate, which, although readily soluble, form comparatively pale-coloured solutions. The acetate and propionate give dark and fairly strong solutions, but secondary reactions occur on electrolysis, a coating of basic salt being deposited on the gelatin.

On the view now suggested, dyad copper, or copper in an ordinary

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* A certain amount of the solution enters the gelatin by ordinary diffusion, and masks the presence of the dark ion, if this exists only in a small quantity: but with the glycerate and lactate the transference towards the positive electrode seems to be greater than that accountable for by diffusion, indicating the passage of some blue anion.

hydroxyl group, has always in solution the same colour intensity (unity), whilst tetrad copper, or copper in the electronegative portion of the molecule, has an intensity about nineteen times greater: the co-existence of these two forms of compounds in solutions of organic copper salts explains, not only the colour phenomena, but the results obtained on electrolysis also, since the cupri-compound would dissociate into $R_2{}'\overset{-}{\mathrm{Cu}}''''\mathrm{O}\,|\,\overset{+}{2}\mathrm{H}$.*

These two forms of copper salts have actually been isolated in the case of the glycerate and racemate, under circumstances which, as regards the glycerate, preclude the cupri-compound form being a mere hydrate of the ordinary salt, and they are distinguished by differences of solubility, and by different decomposition temperatures (this vol., p. 176). They are also capable of independent existence as such in solution, and it is found that the solutions exhibit differences in colour intensity in full accordance with the views developed above. The values for crystallised copper glycerate have been entered in table II, and show a variation from 3·4 to 2·1 with increasing dilution, these values being deduced from very concordant series obtained from four different preparations of the salt, deposited on keeping for some days a solution of the cupriglycerate. The cupriglycerate, obtained by precipitating with alcohol or ether a solution of copper carbonate in glyceric acid, possesses a colour intensity about three times greater, ranging from 10 to about 5. The results with four different preparations are given in an abridged form in table IV, the variations between them being, no doubt, attributable to the glyceric acid having been heated to different extents during the dissolution of the carbonate, it not having been ascertained until subsequently that the cupriglycerate is changed by heat into copper glycerate. All these preparations were dried in a vacuum, and then at 100°, before

TABLE IV.

Colour Intensity of Cupriglycerate.

Gram of copper in 100 c.c.	Precipitated by				
	Alcohol.	Alcohol.	Alcohol.	Ether.	Mean.
1·0	9·2	9·5	(12·4)	9·3	10·3
0·4	8·2	9·3	10·1	9·0	9·1
0·1	8·5	8·8	8·3	8·1	8·7
0·04	8·3	9·0	8·2	7·5	8·4
0·01	7·7	8·1	6·6	6·0	7·1
0·002	—	6·7	5·1	4·9	6·0

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* The hydrogen is not in a carboxyl group, and does not, therefore, imply acidity: at any rate, as the copper is in the anion, there is no element but hydrogen which could form the cation.

being used for the colour determination. In solutions stronger than those here entered, the colour is too dissimilar from that of the sulphate to admit of accurate measurement.

The transformation of the cupriglycerate into the normal glycerate, which in strong solution is accompanied by the crystallisation of the latter, can be followed in weaker solutions by the change of colour. A solution of the cupriglycerate containing 0·03 gram of copper per 100 c.c., and possessing a colour intensity of 6·4, showed the following colour intensity:

After heating to boiling	4·5
,, boiling 15 minutes	2·9
,, ,, 30 ,,	2·85

indicating that 47, 85 and 86 per cent. of the total change possible had occurred. A similar change takes place at lower temperatures: the same solution after one week at 10° showed a colour intensity of 4·1 (56 per cent. of total possible change), and after three weeks an intensity of 3·1 (83 per cent.). This instability of the cupri-compound in solution would fully account for these solutions never showing a colour intensity as high as the 19 attained in other cupri-compounds, although some of the cupri-salt would always be present in the solution, preventing the colour intensity from falling to unity. The dry salt itself is not stable: a specimen which had been kept for a year showed a reduction of about half in its colour intensity when dissolved. But water favours the change, and this is in accordance with the diminution in colour intensity observed when solutions of organic copper salts are diluted.

A similar change on heating appears to occur in the case of a solution of the malate, but as the colour intensity was reduced by only about 10 per cent., this cannot be regarded as established. With the citrate and phthalate, which are also highly coloured in solution, a basic salt is precipitated on heating. No change occurred with the lactate.

It is probable that some of the so-called normal salts are really the corresponding cupri-compounds. Nearly all the copper salts of organic acids are characterised by sparing solubility in water, the most soluble being the propionate, dissolving to the extent of 3·8 grams of copper per 100 c.c., whilst many of them are nearly or quite insoluble (see Trans., 1912, **101**, 184). Their solutions are stable at the ordinary temperature, and the addition of alcohol causes a gradual separation of the salt in a crystalline condition (except with the salts of the higher members of the fatty acids, which are more soluble in alcohol than in water). In strong contrast with these, we have the citrate, malate and glycerate, which are all excessively soluble, apparently infinitely so, and are all precipitated by alcohol from their solutions in the form of emulsions. Since the glycerate in question has been found to be the cupri-compound, the natural inference is that the other two, also, are cupri-compounds.* They both possess an exceptionally high colour intensity in solution, and strong solutions of them decompose after a time, but they deposit basic salts, instead of the normal salt, as in the case of the glycerate.

Whether the deep coloration of the various compounds examined should be regarded as due to the copper in them being quadrivalent, or to its being in the electronegative portion of the molecule, is not certain; but the former explanation appears preferable. In the entries Nos. 1, 2, 3, 11, 12, 13, 16, 18, 19, 20, 21, 23, 24 and 25 in table III the formulæ suggested for the compounds contain nothing but quadrivalent copper; in Nos. 6, 7 and 8 they have been represented as containing the groups $CH(Cu''OH)$; in Nos. 5, 17 and 22 the group $\vdots C{<}\genfrac{}{}{0pt}{}{O}{O}{>}Cu''$, and in Nos. 9, 10, 14 and 15 the group $\genfrac{}{}{0pt}{}{\cdot O\cdot Cu''\cdot O\cdot}{\cdot O\cdot Cu''\cdot O\cdot}$. In the last case the copper atoms would be quadrivalent if united to each other, and in the other two such a union could occur if the minimum formulæ were doubled. Such duplication seems to be required in several instances owing to the proportion of water present in the compounds, and, as previously pointed out, it is in accordance with the ease with which these substances liberate cuprous oxide. That a considerable increase in colour intensity should accompany the change in function of an atom from a dyad to tetrad is further rendered probable by the analogous behaviour of the allied elements, iron and manganese, and such a change is, indeed, only an extension of the phenomena already presented by copper itself, when the univalent (or pseudo-univalent) † and colourless atom in the cuprous salts becomes highly coloured on its assumption of bivalent functions. Judging by the ferrocyanides, great increased depth of colour is not correlated with a position in the electronegative portion of a molecule.

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* This has now been established as regards the malate.

† According to Bodländer and Storbeck (*Zeitsch. anorg. Chem.*, 1902, **31**, 458) the cuprous ion is Cu , not $(Cu_2)''$.

CLXXVII.—*The State of Amines in Aqueous Solution.*

By Tom Sidney Moore and Thomas Field Winmill.*

The experimental work now described was undertaken to test the applicability of a method for determining the equilibrium constants of pseudo-acids and pseudo-bases in solution; ammonia and the amines in general furnish a good example of the latter type. The hydrate formed on dissolving an amine in water dissociates into an alkylammonium and an hydroxyl ion, neither hydration nor ionisation being complete. Representing the equilibrium by the equations:

$$NX_3 + H_2O \rightleftharpoons NX_3H(OH) \rightleftharpoons NX_3H' + OH';$$
$$k_1 C_{NX_3} = C_{NX_3H(OH)} \text{ and } k_2 C_{NX_3H(OH)} = C_{NX_3H} \times C_{OH'}.$$

k_1 and k_2, the hydration constant and the true ionisation constant, are obtainable from the apparent dissociation constant and the partition-coefficient of the amine, both measured at three different temperatures (Moore, Trans., 1907, **91**, 1373).† This is the only available method for determining these equilibrium constants, and, in view of its importance and of the incomplete and untrustworthy nature of the existing data, the velocities of the amine ions, the apparent dissociation constants, and the partition-coefficients of ten amines have now been determined at 18°, 25°, and 32·35°, these temperatures having been chosen for reasons given on p. 1663.

This paper divides itself naturally into two parts:

Part I (by Winmill) consists of a description of the experimental method for the determination of the apparent ionisation constants and the partition-coefficients, with a discussion of the results of the measurement. A summary of this part will be found on p. 1663.

Part II (by Moore) contains a discussion of the method for

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* For abstracts, see Proc., 1912, **28**, 109, 126.

† The following are the corrections of the misprints in this paper:

Page 1375, at the bottom of the page, *for* $\log_e \frac{}{k'_1}$ *read* $\log_e \frac{k''_1}{k'_1}$.

Page 1376, 11th line from bottom, *for* $\frac{t_1^2}{t_2^2} = S_1$ and $\frac{t_2^2}{t_3^2} = S_2$ *read* $\frac{z_1^2}{z_2^2} = S_1$ and $\frac{z_2}{z_3^2} = S_2$.

Page 1376, equation (15), *for* $\frac{y_1}{y_2} = \frac{t_1^2}{t_2^2} \frac{k'_1}{k'_1}$ *read* $\frac{y_1}{y_2} = \frac{z_1^2}{z_2^2} \frac{k''_1}{k'_1}$.

Page 1377, equation (19), the denominator of the right-hand member is $a_2 - z_2 - r_2 n(a_3 - z_3)$.

Page 1377, equation (21*a*), the left-hand member is $\frac{K'}{K''} \frac{1 + k'_2}{1 + k''_2}$.

calculating the true ionisation constants and hydration constants from the experimental results, and the results of the calculation. These results lead to new methods of formulating quinquevalent nitrogen compounds. A summary of Part II is given on p. 1676. The actual experimental work was carried out almost entirely by Winmill.

PART I.

The complexity of the quantitative relations between the degree of hydration and of the true ionisation and the experimental results necessitates the attainment of a high degree of accuracy in the latter, and the attempt was made to ensure that they should be accurate to one part in 1000. Such accuracy seems, however, unattainable in conductivity measurements owing to many uncertainties in "standard values," discussed below; it is also greater than experimental difficulties permit in determining partition-coefficients.

The following units and symbols are used in the description of the work: K_c = cell constant; η = concentration in gram-equivalents per c.c.; R = resistance in ohms; $\mu = K/R\eta$ = molecular conductivity in reciprocal ohms (mhos.); α = the degree of ionisation; $K = \alpha^2/(1-\alpha)$ = the apparent dissociation constant. The slope of the line connecting molecular conductivity with the square-root of the dilution is given by $\Delta = \mu_{\infty} - \mu_{\eta=10^{-6}}$, and the partition-coefficient is the concentration in the aqueous layer divided by that in the non-aqueous layer.

The Materials Used.

Water.—The fraction of water from the laboratory still which showed no evidence of containing ammonia with Nessler's reagent was distilled in apparatus similar to that of Hartley, Campbell, and Poole (Trans., 1908, **93**, 428). Each distillation yielded 3 litres of water of conductivity $0{\cdot}7 \times 10^{-6}$ mhos.; the conductivity was at first often as low as $0{\cdot}5 \times 10^{-6}$ mhos., but this value rapidly rose to $0{\cdot}7 \times 10^{-6}$. For the storage of the water borosilicate glass flasks were used; these were fitted with ground-on caps with sealed-on capillary tubes, which could be connected to an air-pump. The water is thus prevented from absorbing air, and unless this is done minute air bubbles are apt to form on the electrodes of the cells; these bubbles are difficult to remove, and, being small, they are frequently only detected by their effect on the resistance of the solution.

Amine Hydrochlorides.—The hydrochlorides obtained from Kahlbaum, or prepared from the purchased amines, were crystallised from alcohol, and the various fractions dried in desiccators containing concentrated sulphuric acid and solid potassium hydroxide. The purity of the product was tested by determining the conductivity of each fraction after repeated crystallisation in the cases of methylamine and dimethylamine hydrochlorides; as successive fractions gave identical results, it was only considered necessary to recrystallise each of the other hydrochlorides twice.

Solutions of the Free Amines.—These were prepared from the hydrochlorides or the acid oxalates in the following manner: A 0·1 per cent. solution of potassium hydroxide in water of conductivity $1{\cdot}0-2{\cdot}0\times10^{-6}$ is boiled in a large Jena-glass flask, and the steam, trapped by passing through glass-wool, condensed in a tin condenser tube; the distillation is continued until the conductivity of the distillate falls to $1{\cdot}0-1{\cdot}5\times10^{-6}$. A Jena-glass flask, carrying a soda-lime tube, is then attached to the end of the condenser, and a solution of the amine hydrochloride or oxalate run into the boiling potassium hydroxide solution through a dropping funnel; the amine distils in the steam, and a solution free from carbon dioxide is obtained in the receiving flask. The concentration of amine in these solutions was estimated by weight titration, with standard hydrochloric acid solution, the concentration of which in gram-molecules per kilo. of solution was estimated by two methods, namely, Masson's Iceland spar method, and by precipitation of the chlorine by silver nitrate and weighing the silver chloride produced.

To carry out the titration of the amine solution two weight pipettes were used, one containing the amine solution approximately $N/5$, the other the acid. After these have been weighed a quantity of acid is run from the pipette into a stoppered flask, and one drop of methyl-red solution added. The amine solution is now added until the methyl-red just changes colour. The addition of another drop of acid produces a faintly acid solution. This excess of acid was titrated by an $N/100$-sodium hydroxide solution, delivered from a burette graduated in 1/20ths c.c. With practice this "back" titration never uses more than 0·2 c.c. of the alkali solution. All estimations were done in duplicate; the difference between the two did not ordinarily exceed 1 in 3000.

Apparatus.

The electrical conductivity of the solutions used was measured by the usual bridge and telephone method, with an alternating current. The bridge wire was stretched between ebonite supports, and connected to them by 5—6 cm. of waxed silk, and was so arranged as to reduce the effects of self-induction to a minimum. The middle, on which the sliding contact moved, was of platinum-iridium; the ends were of manganin, thickly coated with paraffin-wax. By having a comparatively short platinum wire the temperature-coefficient of the resistance (and hence of the length of the bridge) is reduced to a minimum. The platinum wire was kept stretched by a hanging weight, and was 8 cm. above the wooden bed of the bridge. In this way a very complete insulation is obtained, since leakage can only take place over the waxed silk or the ebonite, both excellent insulators. The resistance box and the conductivity cell were connected to the bridge by switches so arranged that the positions of the cell and resistance box with respect to the bridge could be interchanged. By this means, when a resistance was being measured a balance point could be taken on either side of the centre of the bridge, eliminating any accidental asymmetry. The resistance box contained manganin coils which had been carefully calibrated.

The *thermostat* was a large asbestos-covered cylindrical bath, filled with water stirred by an electric motor. The heating was electrical, and the temperature was regulated by a Lowry regulator holding 450 c.c. of toluene. The temperature variation at the three temperatures used was $\pm 0{\cdot}005^\circ$. The thermometers were calibrated against standard thermometers corrected to the hydrogen scale, which were kindly lent by Mr. H. Hartley.

The conductivity cell (for the loan of which we have also to thank Mr. Hartley) was made entirely of borosilicate glass, and consisted of a pear-shaped flask holding 280 c.c. fitted with a ground-on cap. Into this cap were sealed the glass tubes holding the electrodes, a three-way tap, and a short tube closed with a ground-on stopper. The electrodes were of stout platinum 2—3 mm. apart, measuring 2×3 cm. Each was perforated by six holes, which were not set symmetrically, so that by rapidly rotating the cell cap the solution in the cell was efficiently stirred. The electrodes were covered with a grey platinum surface, which is to be preferred to black in that it shows no tendency to absorb salts from the solution in the cell, and is not easily rubbed off (compare Whetham, *Phil. Trans.*, 1900, **194**, 324). It further has the advantage that the oxidation of an amine which is liable to take place in the presence of platinum-black does not take place with grey platinum. The cell was tested as to the solubility of the glass, and the possible contamination of the solutions by slow air leakages by allowing water to remain in it for fourteen days. The initial conductivity of the water was $1{\cdot}0 \times 10^{-6}$ mhos. At the end of the time it was $1{\cdot}2 \times 10^{-6}$ mhos., a rate of variation quite negligible.

The cell was cleaned before an experiment by washing with conductivity water ($1{\cdot}0 \times 10^{-6}$ mhos.). The flask part was then dried at 120°. The cap was dried with filter paper, and then air-dried to constant weight.

The method of weighing described by Manley (*Phil. Trans.*, 1910, **210**, 381) has been followed throughout, so far as the weights are affected to 0·1 milligram. The weights used were calibrated, and all weighings quoted have been corrected for air displacement.

Preparation of Conductivity Solutions.—The usual method of preparing a series of solutions for conductivity measurements is to make up the strongest solution it is desired to measure, and from it, by means of volume dilutions, to prepare a series of weaker solutions. The great difficulty of pipetting small quantities of solution with accuracy and the certainty of contamination of the solution by impurities from the air, make this method very unsatisfactory, even for salt solutions, and render it useless in the case of bases.

The weakest solution is always measured last, and there is no way of ascertaining what part of the conductivity of the solution is due to impurity in the water used. These possibilities of error are reduced to a minimum in the method adopted in the present work (compare Whetham, *Phil. Trans.*, 1900, **194**, 330). A solution of the hydrochloride or amine is transferred to a weight pipette, which is completely filled. The conductivity cell is filled with a weighed quantity of water, and allowed to remain in the thermostat for one hour. The conductivity of the water is then measured. A small quantity (from 0·3 to 0·5 gram) of the $N/5$-hydrochloride or amine solution is then added to the cell through the small side-tube in the cap. The cell is well shaken and allowed to remain in the thermostat for half an hour. The solution is then well stirred by revolving the cell cap, and the conductivity measured; after an interval of fourteen minutes the contents of the cell were again stirred and the conductivity measurement repeated. The most dilute solution to be measured is always prepared from water of which the conductivity has just been determined. Weighed quantities are used instead of less accurate volume measurements. These have, of course, to be corrected to volume relations finally; in all the solutions dealt with the density has been taken to be that of water at the same temperature. The density of the hydrochloride solutions was not determined; that of the amine solutions was, but was never such as to affect the results by 1 per 1000.

During preliminary experiments pure carbon dioxide-free air was passed through the cell while an addition was being made. Further experience showed that this was unnecessary. The average time taken to make an addition was half a minute. The small side-stopper could be left off for five minutes without affecting the conductivity of even an amine solution.

The Cell Constant.

For the determination of the constant of the cell a series of conductivities of potassium chloride was measured exactly as described above. The values of $1/R\eta$ so obtained were plotted against the square-root of the concentration. The comparison of corresponding points on this curve and Kohlrausch's curve for the molecular conductivity of potassium chloride gives the cell constant. The constancy of the constant taken at various points between $N/250$ and $N/2500$ shows the trustworthiness of the determination. the cell was re-standardised about once a week while the experiments were in progress, but no variation was ever detected.

Values of Conductivity of Potassium Chloride Solutions.

The most satisfactory values for the molecular conductivity of potassium chloride are the following:

At 18°.—The values given by Kohlrausch (Kohlrausch and Maltby, *Wiss. Abhandl. der Reichsanstalt*, 1900, **3**, 154).

At 32·35°.—The only numbers at this temperature are those calculated from the Kohlrausch values at 18° by means of Desguine's temperature-coefficient (*Diss.*, Strasburg, 1895, "Temperatur und Leitvermögen").

At 25°.—There is a large number of determinations by different experimenters at this temperature, which differ considerably from one another. Kohlrausch's measurements refer only to $N/100$, and the resistance of such a solution in the cell used being very small, this point could not be used for the determination of the cell constant. The numbers of Ostwald, Boltwood, Bredig, Walden, and Kohlrausch were all plotted together, and the curve passing through the greatest number of points was drawn. The conductivities of eight potassium chloride solutions were then measured, and the constant of the cell calculated from the curve just described. If this curve had the wrong slope, it is obvious that the values found for the cell constant would not have been constant, but would have shown a definite variation. As experiments gave identical results at all dilutions, there is every reason to suppose that the curve values taken are correct.

Determination of Molecular Conductivities of Amine Hydrochlorides.

The series of dilutions necessary for the determination of the molecular conductivity of the amine hydrochlorides at infinite dilution were made in the manner before described. Measurements of resistance were always made with two sets of coils from the resistance box and two reversals of the position of cell and box. As an example of the method, the measurements made with methylamine hydrochloride solutions at 18° may be quoted:

TABLE I.

No. of solution.	Resistance in box.	Position of cell.	Balance point on bridge.	Resistance of cell.	Mean.
1	460	R	25·4	458·1	458·1
		L	25·00		
	455	L	24·85	458·1	
		R	25·50		
2	160	R	25·0	160·5	160·5
		L	25·3		
	161	L	25·0	160·5	
		R	25·3		
3	118	R	25·0	118·4	118·4
		L	25·3		
	119	L	24·9	118·4	
		R	25·4		
4	94	R	24·8	94·69	94·70
		L	25·5		
	95	L	25·0	94·70	
		R	25·3		

The values of the molecular conductivities of the hydrochlorides from $N/300$ to $N/3000$, plotted against the square root of the concentration in gram-equivalents per c.c., lie on straight lines, from which the conductivity at infinite dilution is obtained. It is well known that the slope of the conductivity curves for members of a similar group of salts at the same temperature is constant. This is the case with the amine hydrochlorides. The mean slope Δ from $\sqrt[2]{\eta}=0$ to $\sqrt[2]{\eta}=10^{-3}$, that is, from $N/0$ to $N/1000$ is, at 18°, 2·65; at 25°, 2·88; at 32·35°, 3·55.

Corrections to be Applied to the Measurements.—These corrections are required for (1) the effects of the conductivity of the water; (2) the effect of viscosity; (3) the effect of possible hydrolysis of the amine hydrochlorides.

Effect of Water Conductivity.—The measured conductivity of a salt solution in water is too high, since the water initially has a conductivity. This is best allowed for in the case of hydrochlorides by simply subtracting the specific conductivity of the water from that directly measured for the solution. The true specific conductivity so obtained divided by η gives the molecular conductivity.

The water correction which assumes the above simple form in the case of hydrochlorides becomes much more complicated when the dissolved electrolyte is a base. The nature of the impurities present in conductivity water has been studied very fully by Kohlrausch

(*Zeitsch. physikal. Chem.*, 1894, **14**, 321). The conclusion reached was that water which comes into contact with air must have a minimum conductivity of $0{\cdot}6 \times 10^{-6}$ mhos. at 18°, owing to absorption of carbon dioxide.

Walker and Cormack (Trans., 1900, **78**, 5) have confirmed this by an independent method. They measured the dissociation constant of carbonic acid, and from this and Bunsen's value for the coefficient of absorption of carbon dioxide by water, together with the partial pressure of carbon dioxide in the air, conclude that if Henry's law is obeyed, the conductivity of water will be $0{\cdot}605 \times 10^{-6}$ on account of absorbed carbon dioxide. In addition, Kohlrausch and Maltby (*loc. cit.*) find that the temperature-coefficient of water distilled in a vacuum and allowed to rise in conductivity to $0{\cdot}6 \times 10^{-6}$ mhos. in air, is the same as a solution of carbon dioxide. The water used in the present experiments had a conductivity of 0·7 (at 18°) immediately before being put into the conductivity cell, where it usually rose to $1{\cdot}0 \times 10^{-6}$, due, no doubt, to the impossibility of cleaning and drying the cell without introducing minute traces of electrolytes. It is fairly safe, therefore, to assume that $0{\cdot}6 \times 10^{-6}$ mhos. at 18° of this conductivity is due to dissolved carbon dioxide. The difference between this and the observed conductivity has been taken to be due to dissolved salts; this part has been allowed for by subtraction, as in the case of the hydrochlorides.

The amine and carbon dioxide will, however, combine to form a carbonate, which—both acid and base are weak—is capable of being hydrolysed to a considerable extent. It is necessary to know exactly what happens in order to calculate the effect on the resistance of the solution.

Both carbonate and hydrogen carbonate may be formed, and both of these may be hydrolysed. Since both acid and base are weak, we may assume that the free acid and free base produced by the hydrolysis are not ionised, but that the salt is completely ionised at the dilution considered. At equilibrium we shall have in solution: X_3NH', CO_3'', HCO_3', H', OH' as ions, and H_2CO_3 and X_3NHOH undissociated. Hence:

$$C_H \times C_{HCO_3}/C_{H_2CO_3} = k_1\ ;\ C_H \times C_{CO_3}/C_{HCO_3} = k_2\ ;\ C_H \times C_{OH} = k_w\ ;$$

where k_1 and k_2 are the first and second dissociation constants of carbonic acid, and k_w is the dissociation constant of water. From these equations we get

$$C_{H_2CO_3}/C_{HCO_3} = k_w/k_1 \times C_{OH}.$$

All the quantities on the right-hand side of these two equations are known. For k_1 see Walker and Cormack (*loc. cit.*); for k_2, M'Coy (*Amer. Chem. J.*, 1907, **29**, 437).

The concentration of the hydroxyl ion can be deduced, with much greater accuracy than is required for the correction, from the conductivity measurements of the amine solutions under discussion. The ratio of the concentrations of the undissociated carbonic acid and the ions HCO_3' and CO_2'' can therefore be calculated. Since the concentration of carbon dioxide in conductivity water is $1{\cdot}25 \times 10^{-8}$ gram-molecule per c.c. (Walker and Cormack; Kohlrausch, *loc. cit.*), the absolute concentrations of the three forms can also be determined. The carbonic acid may be regarded as practically undissociated, hence all the ions CO_3'' and HCO_3' will be derived from the completely dissociated carbonate and hydrogen carbonate formed. The concentration of these ions gives, therefore, the concentration of the salts formed.

The ratio $C_{H_2CO_3}/C_{HCO_3}$ will be greatest in the case of the weakest base, namely, ammonia, and at 18° is equal to $3{\cdot}4 \times 10^{-5}$. Where the concentration of carbonic acid is greatest, therefore, it is only 1/30,000 that of the HCO_3, and may be neglected. Hence all the carbon dioxide of the water is present as carbonate and hydrogen carbonate in the amine solutions considered.

The method of applying these results may best be followed by taking a concrete example. For methylamine at 18°:

$$C_{CO_3}/C_{HCO_3} = 22{\cdot}91.$$

Since $C_{CO''_3} + C_{HCO'_3} =$ concentration of carbon dioxide in the water $= 1{\cdot}25 \times 10^{-8}$. $C_{CO''_3} = 1{\cdot}20 \times 10^{-8}$ gram-molecule per c.c. $= 2{\cdot}40 \times 10^{-8}$ gram-equivalent per c.c. $C_{HCO'_3} = 0{\cdot}05 \times 10^{-8}$ gram-molecule per c.c. $= 0{\cdot}05 \times 10^{-8}$ gram-equivalent per c.c.

Solutions of these strengths of methylamine carbonate and methylamine hydrogen carbonate have specific conductivities of 2·94 and 0·04 gemmhos respectively. The water initially had a specific conductivity of 0·91 gemmhos, of which 0·6 has been taken as being due to carbon dioxide, leaving 0·31 as due to dissolved salts. The total conductivity due to substances other than methylamine hydrate is therefore 3 29 gemmhos. The specific conductivity of the solution as measured was 542·01 gemmhos. The true specific conductivity is therefore 538·72 gemmhos.

There is still a further correction to be made. The effective concentration of amine is also changed, since some has been used to form a salt of which conductivity has been subtracted. The quantity used is clearly the sum of the concentration of the carbonate and hydrogen carbonate in gram-equivalents per c.c., that is, $(2{\cdot}4 + 0{\cdot}05) \times 10^{-8} = 2{\cdot}45 \times 10^{-8}$. This quantity must be subtracted from the observed concentration.

Effect of Viscosity of the Solution.—It has been suggested (Bousfield, *Zeitsch. physikal. Chem.*, 1905, **53**, 257) that the velocity of an ion is inversely proportional to its size and to the viscosity of the solution. The hypothesis is only in part theoretical, and is in part empirical. Experiment has shown that some such correction must be applied, and that the best method of doing so is to multiply the observed conductivity by the viscosity of the solution (compare Hartley, Applebey, and Thomas, Trans., 1908, **93**, 538; Sidgwick and Rivett, Trans., 1910, **97**, 736; Pusarzewsky and Lemcke, *Zeitsch. physikal. Chem.*, 1905, **52**, 479). This correction does not affect the hydrochlorides, since the solutions were so dilute that the viscosity was that of water. It does, however, become important in the stronger amine solutions. The viscosities of these solutions were measured in duplicate in two Ostwald viscometers. It was found that the relative viscosity, compared with that of water of such dilute solutions of any particular amine, is practically the same at the three temperatures considered.

The corrected molecular conductivity of an amine solution is therefore:

$$= \frac{\text{corrected specific conductivity} \times \text{viscosity.}}{\text{corrected concentration}}$$

Effect of Hydrolysis of Amine Hydrochlorides.—The amines are generally known as "weak" bases; it is therefore necessary to see how far it is possible for the hydrochlorides to be hydrolysed in aqueous solution, and how far the hydrolysis affects the value of the molecular conductivity as deduced from the conductivity of the hydrolysed solution.

If x = fraction of total salt hydrolysed; v = volume of water in c.c. containing 1 gram-equivalent of the salt; K = apparent dissociation constant of the amine, and k_w that of water, then $k_w/K = x^2/v(1-x)$. Applying this formula to the most dilute solutions of the hydrochloride of the weakest base (trimethylamine), the values of $X \times 10^4$ are: at 18°, 5·7; at 25°, 5·0; at 32·35°, 5·4.

If η = the concentration of the hydrochloride the specific conductivity due to the hydrogen ion at 18° is $318 \times \eta \times X$. Similarly the specific conductivity of the displaced trimethylammonium ion is $41{\cdot}4 \times \eta \times X$. The total excess in the observed conductivity at 18° is therefore $1{\cdot}6 \times 10^{-6}$; this must be subtracted from the observed to give the true value. Table II gives the results of correcting the observed trimethylamine hydrochloride results.

TABLE II.

$(CH_3)_3NHCl$.

t.	$\eta \times 10^6$.	$K_c/R\eta$ obs.	$K_c/R\eta$ corrected for hydrolysis.
18°	0·0	106·95	106·75
	0·3501	105·35	105·14
	0·9744	104·30	104·16
	1·3311	103·88	103·76
25°	0·0	125·04	124·8
	0·6553	122·41	122·24
	1·6131	120·92	120·84
	1·8027	120·81	120·70
	2·1015	120·34	120·25
	2·7483	119·50	119·43
32·35°	0·0	144·28	143·85
	0·8254	141·08	140·86
	1·4129	140·26	140·10
	2·0763	139·40	139·27
	3·0793	138·03	137·92

Discussion of Results.

I.—*Molecular Conductivities of the Amine Hydrochlorides.*

The values for the conductivity at infinite dilution are given in the following table. These numbers are extrapolated from the experimental results by plotting the molecular conductivity against the square-root of the concentration in gram-equivalents per c.c. The numbers given are believed to be accurate to 1 in 500. The only other systematic measurements are due to Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 191), who, however, only worked at 25°. His values have been recalculated in terms of the standard reciprocal ohm now in use.

TABLE III.

	18°.	25°.	32·35°.	Bredig, 25°.
$CH_3 \cdot NH_3Cl$	116·9	136·1	156·5	136·0
$(CH_3)_2NH_2Cl$	111·1	129·0	149·3	127 9
$(CH_3)_3NHCl$	106·7	124·8	143·8	124·5
$C_2H_5 \cdot NH_3Cl$	104·7	123·2	143·2	124·4
$(C_2H_5)_2NH_2Cl$	97·5	113·9	132·9	113·1
$(C_2H_5)_3NHCl$	94·3	110·2	127·8	109·3
$C_3H_7 \cdot NH_3Cl$	100·5	117·8	137 0	117·2
$(C_3H_7)_2NH_2Cl$	91·95	108·2	125·2	106·9
$(C_3H_7)_3NHCl$	88·82	103·2	118·6	101·8

There seems to be no regular change in the value of the molecular conductivity corresponding with a definite change in molecular weight and structure, nor is there a regular difference between primary, secondary, and tertiary amine hydrochlorides. The conductivity does not always fall as the molecular weight rises, for example, ethylamine hydrochloride has a lower conductivity than triethylamine hydrochloride, which has a higher molecular weight. Among the isomerides there appears to be a regularity at 18°; the ratio of the conductivities is constant:

$$(1)\ \frac{\mu(CH_3)_2NH_2Cl}{\mu(C_2H_5)NH_3Cl}=1{\cdot}061. \qquad (2)\ \frac{\mu(CH_3)_3NHCl}{\mu(C_3H_7)NH_3Cl}=1{\cdot}062.$$

$$(3)\ \frac{\mu(C_2H_5)_3NHCl}{\mu(C_2H_7)_2NH_2Cl}=1{\cdot}062.$$

That this relation is purely accidental is shown by a comparison of the same ratio at 25° and 32·35°:

	25°.	32·35°.
(1)	1·049	1·043
(2)	1·066	1·050
(3)	1·020	1·020

The Variation of Conductivity with Temperature.

The variation of the conductivity of electrolytes with varying temperature has been the subject of much investigation. A very complete list of references to the literature on the subject is given by Jones and West (*Amer. Chem. J.*, 1905, **27**, 357) and Bousfield and Lowry (*Proc. Roy. Soc.*, 1902, **71**, 42). References to all the papers mentioned below will be found in these two accounts.

Ohm appears to have been the first to notice that the resistance of an electrolyte varied with the temperature of the solution, but it was not until thirty years later (1874) that any systematic investigation of the variation was made, when Grotrian represented the conductivity of sulphuric acid solutions by

$$\mu_t=\mu_o(1+at+bt^2),$$

and that of hydrochloric acid by

$$\mu_t=\mu_o(1+at),$$

where t = temperature in degrees Centigrade, and a and b are constants. Grotian a year later, with Kohlrausch, investigated a few more cases, and decided that the first formula in general represented the observed results.

From this time until 1895 many measurements were made, but no important results were obtained.

In 1895 Désguine measured the conductivities of a number of salts between 2° and 35°, and expressed his results in the form

$$\mu_t=\mu_{18}[1+a(t-18)+b(t-18)].$$

The temperature is expressed in degrees Centigrade, and a and b are constants.

It is from these measurements that the temperature-coefficients of the conductivities of the ions given by Kohlrausch and von Steinwehr (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, **26**, 570) are calculated.

Kohlrausch has pointed out that these coefficients lead to zero conductivity for all salts in the neighbourhood of −38°. This was explained by showing that the viscosity of water (on the assumption that the viscosity temperature curve was continuous) becomes infinite at about the same temperature.

Kuntz (*Zeitsch. physikal. Chem.*, 1903, **42**, 591) has measured the conductivity of sulphuric acid solutions as low as −70° without obtaining a zero value. Later observations on calcium chloride and sodium hydroxide also showed that no zero of conductivity could be observed.

Bousfield and Lowry (*loc. cit.*) show from a consideration of the known results that such extrapolation is not warranted, since no conductivity-temperature curve is represented by a simple equation over any but a very small range of temperature. All curves which have been followed over any considerable range show points of inflexion and maxima, thus:

Arrhenius *	H_3PO_4 aq.	shows	maximum at	54°
Maltby †	KCl aq.	,,	,,	237
Noyes and Coolidge ‡...	KCl aq.	,,	,,	280
	NaCl aq.	,,	,,	280

* *Zeitsch. physikal. Chem.*, 1889, **4**, 96. † *Ibid.*, 1895, **18**, 155.
‡ *Ibid.*, 1903, **46**, 323.

In non-aqueous solutions there is even more evidence of maxima and points of inflexion [compare Franklin (solutions in liquid ammonia), Maltby (solutions of hydrogen chloride in ether), Cattaneos (solutions in ether, alcohol, and glycerol), Hagenbach (solutions in liquid sulphur dioxide), Walden and Centnerzwer (solutions in sulphur dioxide), Kraus (solutions in methyl and ethyl alcohol)].

It appears, therefore, that temperature-coefficients of conductivity apply only to the range of temperature over which the measurements have been made, and that extrapolation over a much wider range is not permissible.

Many formulæ were tried to express the results now described; of them all the most satisfactory is

$$\mu_T = \alpha T(1 - \beta T),$$

where T is the absolute temperature, and α and β are constants. This equation only involves two constants, which may be calculated from any two of the measurements, allowing the ionic velocity at the third temperature to be calculated. A table shows that the equation represents the results to 1 in 600.

Variation of Ionisation with Temperature.—In general, rise of temperature seems to cause a decrease in the degree of dissociation of salts (compare Wood, *Phil. Mag.*, 1895, **41**, 117; Schaller, *Zeitsch. physikal. Chem.*, 1898, **25**, 497; Whetham, *Phil. Trans.*, 1900, **194**, 321; Jones and West, *Amer. Chem. J.*, 1911, **34**, 357). Douglas (*Amer. Chem. J.*, 1904, **26**, 428) could find no variation between 0° and 35°. In the present investigation little difference could be detected in the degree of ionisation between 18° and 32·35°. There is, however, some indication of a maximum between these temperatures, as is shown by the following table, which refers to $N/1000$-solutions of the respective salts.

	Degree of ionisation × 1000.		
Hydrochloride of:	18°.	25°.	32·35°.
Methylamine	977	978	977
Dimethylamine	976	978	976
Trimethylamine	975	977	975
Ethylamine	975	977	975
Diethylamine	973	975	973
Triethylamine	972	974	972
Propylamine	974	976	974
Dipropylamine	971	973	972
Tripropylamine	970	972	970

Conductivity of the Ammonium Ions.—The conductivity due to the ammonium ion is the difference between that due to the chlorine ion and the ammonium chloride. To find the ionic mobility, that of the chlorine ion must be known. There is little difficulty in choosing the value to be taken at 18°, Kohlrausch's number, 65·44, being adopted. Noyes and Sammet (*Zeitsch. physikal. Chem.*, 1903, **43**, 63), from a consideration of the latest work on the transport number of the chlorine ion, take a value about 0·2 per cent. higher than that of Kohlrausch. The work on which their conclusion is based seems to be liable to the same errors as Kohlrausch's, and there is no reason for preferring their number.

When the values at 25° and 32·35° are required, however, they have to be calculated by means of Kohlrausch's temperature-coefficients (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, **26**, 570). The numbers so obtained are open to considerable criticism. The sum of the conductivities of the potassium and chloride ions should be equal to the observed conductivity of potassium chloride at infinite dilution. There is, however, a large difference:

	25°.	32·35°.
Calculated conductivity of K′	74·49	84·81
,, ,, Cl′	75·33	85·72
Sum	149·82	170·53
Kohlrausch's experimental values for KCl	150·92	173·4

The calculated values differ from the experimental by 1 per cent. and 2 per cent. at 25° and 32·35° respectively. As to which value is to be taken for the molecular conductivity of potassium chloride, it is clear that the directly determined values are to be preferred to those calculated from a temperature-coefficient determined over a small range of temperature. Since, as has been pointed out, the molecular conductivities of the amine hydrochlorides may be represented at different temperatures by a parabolic formula, it is possible that over the same range of temperature it will also represent those of potassium chloride. If the same formula be applied to the results for potassium chloride, it is found that

$$\alpha = -2{\cdot}0086;\ \beta = 4{\cdot}201 \times 10^{-3}.$$

These give μ_∞ at the three temperatures:

	18°.	25°.	32·35°.
Calculated	130·1	150·8	173·5
Observed	130·1	150·9	173·4

Since, therefore, the relation between temperature and the conductivity of the whole molecule is represented by a parabola, it is impossible that the constituent ions should have linear coefficients, for otherwise a parabola would be the sum of two straight lines.

A parabolic formula for the potassium and chloride ions closely related to Kohlrausch's linear function can be obtained as follows. Suppose the general form used for the hydrochlorides to apply:

$$\alpha t(1-\beta t) = \mu_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Differentiate (1):

$$\frac{d\mu_t}{dt} = \alpha(1-2\beta t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Eliminate α between (1) and (2):

$$\frac{1}{\mu}\ \frac{d\mu_t}{dt} = \frac{1-2\beta t}{t(1-\beta t)}.$$

The quantity $\frac{1}{\mu}\ \frac{d\mu}{dt}$ is the one found by Kohlrausch, hence β can be calculated, and α is found by substituting this value of β in (1), when $t=18°$, or 291 abs.

The deduced equation is only really related to the first when the quantities $d\mu$ and dt are infinitely small; but as the results show, the equations still correspond approximately, even when dt and $d\mu$ have the experimental values. The values given by Kohlrausch (*loc. cit.*) are:

$$\mu_\infty^{18^\circ} \text{ for } \mathrm{K}' = 64{\cdot}67\ \ \frac{1}{\mu}\ \frac{d\mu}{dt} = 0{\cdot}0217$$

$$\text{,,} \quad \text{,,} \quad \mathrm{Cl}' = 65{\cdot}44\ \ \frac{1}{\mu}\ \frac{d\mu}{dt} = 0{\cdot}0216.$$

Substituting these values and solving the equations: for the chloride ion, $\alpha = -0{\cdot}9638$; $\beta = 4{\cdot}238 \times 10^{-3}$; for the potassium ion, $\alpha = -0{\cdot}9589$; $\beta = 4{\cdot}233 \times 10^{-3}$.

From these the values μ_∞ for the two ions can be calculated:

	25°.	32·35°.
K	74·79	85·85
Cl	75·54	86·57
Sum K′+Cl′	150·33	172·4

The difference between the values of the molecular conductivity for potassium chloride calculated in this way and the values found by direct experiment is 1 in 250 at 25° and 1·2 in 200 at 32·35°. As the Kohlrausch temperature-coefficients are only given to 1 in 200, closer agreement would be accidental. There still remains a greater difference than would be expected in the case of the "standard" ions.

The values adopted for the velocity of the chlorine ion are: at 18°, 65·44; at 25°, 75·5; at 32·35°, 86·6. The effect on the amine dissociation constants due to the uncertainty of these values can be calculated, and shown not to exceed 1 in 500. The ionic mobilities for the ammonium ions investigated, together with their temperature-coefficients, are given in table IV.

The Amines.

The dissociation constants of the amines were calculated from conductivity measurements which have already been described. The method of correcting the observed values has also been given.

In the earlier experiments conductivities were measured at several dilutions. In the latter experiments only two solutions were made, at approximately $N/60$. The difficulty of applying suitable corrections for the conductivity of the water renders very uncertain the measurements taken from a range of solutions at great dilutions. At greater concentrations than $N/60$ the viscosity correction becomes of considerable magnitude.

The dissociation constant has been calculated from Ostwald's formula:

$$K = \frac{\eta a^2}{(1 - a)}.$$

In the following table are given the mean of the corrected apparent dissociation constants determined for each amine multiplied by 10^7. The numbers are taken from tables VI, VII, and VIII:

	18°.	25°.	32·35°.
Ammonia	0·1720	0·1805	0·1887
Methylamine	4·589	4·743	4·788
Dimethylamine	6·089	6·354	7·811
Trimethylamine	0·5414	0·6457	0·7997
Ethylamine	5·230	5·198	5·147
Diethylamine	10·59	11·36	11·45
Triethylamine	5·143	5·898	6·661
Propylamine	4·356	4·354	4·304
Dipropylamine	9·157	9·488	9·659
Tripropylamine	—	4·43	—

In every group the secondary amine is the strongest base.

The variation of K with temperature is by no means regular. This is only to be expected, for the apparent dissociation constant depends on two factors:

(1) The variation of the true dissociation constant.

(2) The variation of the hydration of the amine.

In the majority of cases K increases as the temperature rises, but with ethylamine and propylamine it falls slightly. The difference between K_{25} and $K_{32\cdot35}$ is with one exception (diethylamine) greater than that between K_{18} and K_{25}.

Only one tripropylamine solution was measured at 25°. The amine is so sparingly soluble in water that accurate measurements of the dissociation constant or the partition constant is impossible.

Complete details of the experiments with the amine solutions are given in tables VI, VII, and VIII, together with all the dissociation constants.

Partition-coefficients.

In order to obtain sufficient data to determine completely the equilibrium of amines in aqueous solution in addition to the measurements already described, it is necessary to measure at three temperatures the partition-coefficient of the amine between water and a second solvent immiscible with water.

As is well known, if A is soluble in two immiscible liquids, B and C, the ratio of the concentration of A in B to that of A in C is constant when the two solutions are in contact. If, therefore, the amine hydroxide used be insoluble in one of the solvents, the partition-coefficient will be a measure of the quantity of unhydrated amine in the other. Since of the pair of liquids it is necessary for the present investigation that one should be water, the second, which may be denoted by C, must fulfil the following conditions: (1) It must not dissolve the amine hydroxides to any considerable extent. (2) It must be very slightly soluble in water. (3) It must dissolve very little water. (4) The mutual solubilities (2) and

(3) must not vary largely over the range of temperature considered.

It is obvious that these conditions must hold. If the second solvent is soluble to any extent in water, the hydration of the amine will be disturbed. If water is appreciably soluble in C, it will carry over some of the hydrate. The fourth condition must hold also, for the partition is really measured, not between water and C, but between water saturated with C and C saturated with water. Obviously, any considerable variation in solubility over the experimental range of temperatures would have the effect in a smaller degree of changing the solvents.

The auxiliary solvent best fulfilling these conditions is toluene, which, however, cannot be used for ammonia and methylamine; these amines are so sparingly soluble in toluene that an accurate measurement of the partition-coefficient is impossible. In these cases chloroform was substituted for toluene.

The coefficients were determined by shaking an aqueous solution of amine with a convenient volume of toluene or chloroform, and determining the amine concentration in each layer when equilibrium had been reached.

The shaking was done in boro-silicate cylinders closed with two stoppers, which fitted tightly without any lubricant. Experiment showed that equilibrium was always attained in two hours. The cylinders were then allowed to remain in the thermostat for another hour to ensure complete separation of the layers. For removing a known volume of each layer for titration an apparatus was so arranged that the volume removed could be measured before being raised above the level of the water in the thermostat.

The titrations were always carried out by weight in the manner previously described. The estimation of the amine present in the water layer presented no difficulty; in the case of the toluene layer, however, it is a matter of considerable difficulty. Two methods are available, namely, (1) addition of water to the measured volume of toluene, and titration of the mixture; (2) addition of water, then a slight excess of standard acid solution. The excess of acid is then determined by separating the aqueous layer, washing the toluene layer several times with water, and then titrating the whole of the aqueous extract with $N/100$-sodium hydroxide solution.

In theory the first method is quite sound if methyl-orange is used as indicator (methyl-red is almost completely extracted from water by toluene). In practice, however, there is great difficulty in determining the exact end-point. The aqueous layer is apt to become faintly cloudy as the toluene separates, and light is refracted from the upper layer in a very deceptive manner. It was found that the second method gave the best results. In this case sulphuric acid must be used as the standard, since it is much more easily washed out from the toluene. The procedure to be adopted is: To the measured volume of toluene 30 c.c. of water are added, together with 1 drop of litmus; $N/10$-sulphuric acid is then added until the litmus remains red, after the two layers have been well shaken together. A further drop of acid is then added, the flask thoroughly shaken, and the contents transferred to a separating funnel. The aqueous layer is drawn off, and the remaining toluene washed with three quantities of 15 c.c. of water. The aqueous extract is then titrated with $N/100$-sodium hydroxide, using methyl-red as indicator. With practice it is found that the excess of acid will not be greater than is required to neutralise 1·0 c.c. of $N/100$-alkali. After all precautions have been taken it still remains difficult to obtain values for the partition-coefficients as accurate as would at first sight appear possible from the nature of the determination. The numbers given agree in most cases to 1 in 500.

Dawson and McCrae (Trans., 1906, **89**, 1666) have measured the partition-coefficient of ammonia between water and toluene, and in their last list of results claim to have shown that the partition-coefficient varies with concentration. The determinations now described have been made as a rule at a concentration of about $N/10$ in the water layer. At least two concentrations have been used in each case without any sign of variation such as that described by Dawson and McCrae, who give the following numbers for ammonia at 19·5°:

Concentration in aqueous layer.. ...	0·154	0·1885	0·2074	0·336
Partition-coefficient	26·01	25·87	25·92	25·67

Thus, for a two-fold increase in the concentration, Dawson and McCrae find that the constant decreases by 1·5 per cent. We find (table IX):

t°.	Concentration of ammonia in aqueous layer.	Partition-coefficient.
18°	0·07709	27·42
	0·11989	27·44
25°	0·1498	24·23
	0·1987	24·26
32·35°	0·0999	21·20
	0·2420	21·17

In the last case the concentration has increased 250 per cent.

without any change in the partition-coefficient. The numbers for ethylamine, too, support this.

$t°$.	Concentration of ethylamine in aqueous layer.	Partition-coefficient.
32·35°	0·1287	14·76
	0·2479	14·79

The scope of the present work has not permitted a detailed study of these coefficients, but it is intended to carry out a complete series of measurements.

Very few other amine partition-coefficients have been measured. The results of Hantzsch and Sebalt (*Zeitsch. physikal. Chem.*, 1899, **30**, 258) and of Hantzsch and Vagt (*ibid.*, 1901, **38**, 705) are quoted in the following table. The last six numbers are from smoothed curves.

Amine.	Second solvent.	$t°$.	Partition-coefficient.	Now found.
Methylamine	Toluene	0°	7·889	—
		35	2·050	5·996 (32·35°)
Ammonia	Chloroform ...	25	25·1	24·25
Trimethylamine ...	Toluene	18	3·18	3·293
		25	2·35	2·294
		32·35	1·78	1·817
Triethylamine	Toluene	18	0·220	0·1306
		25	0·177	0·0994
		32·35	0·152	0·0694

Except in the case of trimethylamine, the two sets of measurements seem to have little in common.

The figures given in table IX for tripropylamine are only approximate; as was previously pointed out, the amine does not lend itself to accurate measurements owing to its insolubility in water.

The tertiary amines are all more soluble in toluene than the secondary, and the secondary more soluble than the primary, of the same series. Increase in molecular weight is also accompanied by increased solubility in toluene. The change in partition-coefficient is very marked, that of dimethylamine being 8000 times that of tripropylamine. Increase in temperature invariably causes decrease of partition, that is, the solubility increases faster in toluene than in water.

Molecular Conductivities of Amine Hydrochlorides.

I at 18°.

Hydrochloride.	Conductivity of water $\times 10^6$.	$\eta \times 10^6$.	μ.	Δ.
Methylamine	1·24	0·0	116·9	2·66
		0·6437	114·8	
		1·8814	113·1	
		2·5657	112·7	
		3·2302	112·0	
Dimethylamine	0·81	0·0	111·1	2·66
		0·7116	108·8	
		1·3164	107·9	
		1·6278	107·8	
		2·7209	106·7	
Trimethylamine......	0·62	0·0	106·8	2·75
		0·3501	105·1	
		0·9744	104·2	
		1·3311	103·8	
Ethylamine	0·68	0·0	104·7	2·75
		0·3796	103·1	
		0·7013	102·2	
		1·1464	101·8	
		1·5582	101·2	
		2·1182	100·6	
Diethylamine.........	1·03	0·0	97·5	2·60
		0·7240	95·4	
		1·4913	94·4	
		2·2960	93·7	
		3·1496	93·0	
Triethylamine	0·86	0·0	94·3	2·66
		0·5589	92·4	
		1·1961	91·6	
		1·4800	91·4	
		1·7786	90·9	
Propylamine	0·86	0·0	100·5	2·60
		0·4537	98·7	
		1·0101	97·9	
		1·4475	97·3	
		1·8270	97·1	
		2·7746	96·2	
Dipropylamine	0·86	0·0	91·9	2·60
		0·4897	90·2	
		1·0048	89·3	
		1·3080	89·0	
		1·6761	88·7	
Tripropylamine	0·81	0·0	88·8	2·60
		0·6226	86·8	
		1·1184	86·0	
		1·3435	85·8	
		1·6034	85·5	
		2·5417	84·8	

Molecular Conductivities of Amine Hydrochlorides.

II at 25°.

Hydrochloride.	Conductivity of water × 10^6.	$\eta \times 10^6$.	μ.	Δ.
Methylamine ………	2·30	0·0	136·2	2·90
		0·8924	133·5	
		1·6853	132·3	
		2·4233	131·1	
		4·0392	130·4	
Dimethylamine ……	0·95	0·0	129·0	3·05
		0·6434	126·5	
		1·2749	125·6	
		1·8380	124·8	
		2·6267	124·0	
Trimethylamine……	2·27	0·0	124·8	3·10
		0·6553	122·2	
		1·6131	120·8	
		1·8027	120·7	
		2·1016	120·2	
		2·7483	119·4	
Ethylamine………..	1·09	0·0	123·2	2·9
		0·5332	121·1	
		1·2622	120·0	
		2·5160	118·6	
		3·1781	117·9	
Diethylamine ……	1·30	0·0	113·9	2·9
		1·1156	112·0	
		1·5181	110·5	
		2·0767	109·8	
		2·5836	109·3	
		3·2283	108·7	
Triethylamine ……	0·90	0·0	110·3	2·50
		0·7919	107·8	
		1·3343	107·3	
		1·9515	106·4	
		3·1214	105·6	
Propylamine ………	1·20	0·0	117·8	2·8
		0·7040	115·6	
		2·3074	113·5	
		4·2359	112·6	
Dipropylamine ……	1·44	0·0	108·2	3·1
		0·6080	105·9	
		1·0797	105·0	
		1·7993	104·0	
		2·3047	103·4	
Tripropylamine ……	1·50	0·0	103·2	3·1
		0·8872	100·7	
		1·2697	100·1	
		1·9210	99·1	
		2·4725	98·6	
		3·0779	98·2	

Molecular Conductivities of Amine Hydrochlorides.

III at 32·35°.

Hydrochloride.	Conductivity of water × 10^6.	$\eta \times 10^6$.	μ.	Δ.
Methylamine	1·16	0·0	156·5	
		1·0741	153·1	
		1·5273	152·3	3·6
		2·2203	151·6	
		2·8007	151·1	
Dimethylamine	1·40	0·0	149·3	
		1·5824	146·8	
		1·0776	145·8	3·4
		1·7802	144·9	
		2·8986	143·6	
Trimethylamine	1·28	0·0	144·2	
		0·8254	140·9	
		1·4129	140·1	3·5
		2·0763	139·3	
		3·0793	137·9	
Ethylamine	1·09	0·0	143·2	
		1·2511	139·4	
		1·6052	138·9	3·7
		2·0730	138·4	
		2·6936	137·1	
Diethylamine	0·81	0·0	132·9	
		0·2698	130·8	
		0·6546	129·9	3·7
		0·8878	129·4	
		1·8759	127·8	
Triethylamine	0·87	0·0	127·8	
		0·3573	124·6	
		0·9866	124·4	3·5
		1·4401	123·5	
		2·6121	122·0	
Propylamine	1·28	0·0	137·0	
		0·3385	134·8	
		0·7052	133·6	3·5
		1·2129	133·1	
		2·2866	131·5	
Dipropylamine	1·40	0·0	125·2	
		0·4394	122·8	
		0·9098	121·6	3·6
		1·3273	121·0	
		1·9576	120·0	
Tripropylamine	1·35	0·0	118·6	
		0·4509	116·3	3·4
		0·7311	115·9	
		1·5547	114·5	

TABLE IV.

Temperature-coefficients of Molecular Conductivity.

Hydrochloride.	$-\alpha$.	$\beta \times 10^3$.	μ_∞ 18°.	μ_∞ 25°.	μ_∞ 32·35°.
$CH_3 \cdot NH_3Cl$	1·8334	4·1905	116·9	136·1	156·5
			117·0	135·9	156·5
$(CH_3)_2NH_2Cl$	1·8004	4·1639	111·1	129·0	149·3
			110·9	129·1	149·2
$(CH_3)_3NHCl$	1·7422	4·1607	106·7	124·8	143·8
			106·9	124·6	143·9
$C_2H_5 \cdot NH_3Cl$	1·8561	4·1036	104·7	123·2	143·2
			104·7	123·1	143·2
$(C_2H_5)_2NH_2Cl$	1·6895	4·1165	97·5	113·9	132·8
			97·3	114·1	132·6
$(C_2H_5)_3NHCl$	1·5800	4·1415	94·3	110·2	127·8
			94·3	110·2	127·7
$C_3H_7 \cdot NH_3Cl$	1·7449	4·1166	100·5	117·8	137·0
			100·5	117·9	136·9
$(C_3H_7)_2NH_2Cl$	1·5807	4·1264	91·9	108·2	125·2
			92·1	107·9	125·5
$(C_3H_7)_3NHCl$	1·3792	4·1976	88·8	103·2	118·6
			88·9	103·1	118·6

The lower lines of figures in the μ_∞ column are calculated from the given values of α and β.

The values in the upper lines are the experimental results.

TABLE V.

Ionic Conductivities and their Temperature-coefficients.

$v_t = at(1 - bt)$, where t = absolute temperature.

Ion.	$-\alpha$.	$\beta \times 10^3$.	18°.	25°.	32·35°.
NH_4	—	—	63·7	74·4	84·9
$CH_3 \cdot NH_3$	0·8700	4·1381	51·5	60·6	69·9
$(CH_3)_2NH_2$	0·8365	4·0793	45·7	53·5	62·7
$(CH_3)_3NH$	0·8052	4·0420	41·4	49·5	57·7
$C_2H_5 \cdot NH_3$	0·8923	3·9571	39·3	47·7	56·6
$(C_2H_5)_2NH_2$	0·7257	3·9553	32·1	38·4	46·3
$(C_2H_5)_3NH$	0·6162	3·9904	29·1	34·7	41·2
$C_3H_7 \cdot NH_3$	0·7811	3·9690	35·1	42·3	50·4
$(C_3H_7)_2NH_2$	0·6169	3·9484	26·5	32·7	38·6
$(C_2H_7)_3NH$	0·4155	4·1045	23·4	27·6	32·0

In the three following tables:

μ_∞, μ, α, R, and K have the meanings already defined.

S_{H_2O} denotes the specific conductivity of the water used in the experiment. S_{CO_3} denotes the specific conductivity of the amine carbonate present, calculated in a manner already described. S_{HCO_3} denotes the specific conductivity of the amine hydrogen carbonate calculated in the same way.

The numbers used in the calculations are:

[*] Dissociation constant of water at 18·00° $= 0·63 \times 10^{-14}$
25·00 $= 1·1 \times 10^{-14}$
32·35 $= 1·91 \times 10^{-14}$.

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[*] Kohlrausch and Heydweiller, *Ann. Phys. Chem.*, 1894, **53**, 234.

TABLE VI.

Amines at 18°.

Amine.	μ_∞	$\eta \times 10^5$.	R.	$S_{H_2O} \times 10^6$.	$S_{CO_3} \times 10^6$.	$S_{HCO_3} \times 10^6$.	Total $\times 10^6$.	Viscosity.	μ.	a.	$K \times 10^7$.
Ammonia	237·7	1·8087 2·0927	257·20 238·87	0·81	2·89 2·92	0·20 0·20	3·30 3·33	1·000 1·000	7·214 6·724	0·03035 0·02763	0·1718 0·1723
Methylamine ...	225·5	1·4876 1·5654 1·6600	63·482 61·708 59·840	0·91	2·94	0·04	3·29	1·0017 1·0018 1·0019	36·28 35·45 34·51	0·16087 0·15720 0·15302	4·588 4·590 4·589
Dimethylamine	219·7	1·3902 1·5630	59·498 55·773	1·21	2·84	0·04	3·49	1·0014 1·0016	41·40 39·31	0·18846 0·17893	6·085 6·093
Trimethylamine	215·4	1·3286 1·6113	192·19 173·87	0·75 1·15	2·45 2·47	0·11 0·11	2·71 3·13	1·0034 1·0042	13·317 12·126	0·06182 0·05630	0·5412 0·5417
Ethylamine ...	213·3	1·5257 1·6903	62·551 59·190	0·83	2·62	0·04	2·89	1·0036 1·0040	35·99 34·38	0·16872 0·16116	5·227 5·234
Diethylamine...	206·1	1·2872 1·6045	52·131 46·080	1·03	2·47	0·03	2·93	1·0039 1·0049	51·25 46·59	0·24867 0·22601	10·594 10·590
Triethylamine	203·1	1·6738 1·8241	62·959 60·121	0·75	2·40	0·03	2·58	1·0037 1·0041	32·617 31·362	0·16060 0·15442	5·143 5·144
Propylamine ...	209·1	1·6948 1·8845	65·583 61·959	0·86	2·52	0·04	2·82	1·0048 1·0054	30·94 29·48	0·14794 0·14096	4·354 4·358
Dipropylamine	200·5	1·5353 1·6683	51·726 49·420	1·06	2·17	0·02	2·65	1·0049 1·0053	43·37 41·79	0·21624 0·20840	9·160 9·154

NOTE.—When S_{CO_3} and S_{HCO_3} are the same at both dilutions, the numbers are only given once. The column headed "total" gives the specific conductivity to be subtracted from the specific conductivity of the solution.

TABLE VII.

Amines at 25°.

Amine.	μ_∞.	$\eta \times 10^5$.	R.	$S_{H_2O} \times 10^6$.	$S_{CO_3} \times 10^6$.	$S_{HCO_3} \times 10^6$.	Total × 10^6.	Viscosity.	μ.	a.	$K \times 10^7$.
Ammonia	270·3	1·1513 1·3661	303·01 254·52	2·10 1·19	2·76 2·86	0·44 0·40	4·59 3·74	1·000 1·000	10·490 9·655	0·03881 0·03572	0·1804 0·1807
Methylamine...	256·5	1·7452 1·9411	50·577 47·801	0·78	3·37	0·08	3·42	1·0020 1·0022	38·95 37·07	0·15186 0·14452	4·745 4·741
Dimethylamine	249·4	0·2478 0·3219	139·85 119·27	1·00	2·86 2·94	0·19 0·16	3·34 3·39	1·000 1·000	98·27 88·89	0·3941 0·3565	6·352 6·356
Trimethylamine	245·2	0·8233 0·9032	198·61 189·19	1·00	2·64 2·60	0·23 0·22	3·16 3·18	1·0022 1·0024	20·77 19·90	0·08474 0·08116	0·6459 0·6475
Ethylamine ...	243·6	1·4257 1·6070	57·089 53·471	1·09	3·06	0·07	3·51	1·0033 1·0038	42·26 40·07	0·17350 0·16449	5·193 5·203
Diethylamine...	234·3	2·6589 3·2230	29·888 26·888	1·40	2·93	0·03	3·65	1·0081 1·0098	43·632 40·117	0·18622 0·17121	11·340 11·380
Triethylamine..	230·6	1·3072 1·3362	59·804 59·071	1·03	2·76	0·06	3·14	1·0029 1·0030	44·05 43·34	0·19102 0·18923	5·896 5·901
Propylamine ...	238·2	1·3742 1·5993 1·7026	64·602 59·622 57·648	1·06	2·68	0·07	3·09	1·0040 1·0046 1·0049	38·82 36·18 35·16	0·16295 0·15189 0·14763	4·359 4·350 4·353
Dipropylamine	228·6	1·6177 1·6583	43·541 42·955	1·09	2·76	0·15	3·19	1·0051 1·0053	49·06 48·53	0·21462 0·21228	9·488 9·487
Tripropylamine	223·6	0·4054	135·000	1·03	—	—	—	—	62·9	0·282	4·43

Table VIII.

Amines at 32·35°.

Amine.	μ_∞.	$\eta \times 10^5$.	R.	$S_{H_2O} \times 10^6$.	$S_{CO_2} \times 10^6$.	$S_{HCO_3} \times 10^6$.	Total × 10⁶.	Viscosity.	μ.	a.	$K \times 10^7$.
Ammonia	303·8	1·6411	203·98	1·09	2·89	0·61	3·77	1·000	10·13	0·03334	0·1887
		1·8438	192·19		2·93	0·60	3·80	1·000	9·58	0·03153	0·1892
Methylamine ...	288·8	1·8509	43·554	1·16	3·72	0·16	4·22	1·0021	42·87	0·14842	4·788
		1·9928	41·865					1·0023	41·43	0·14345	4·788
Dimethylamine	281·6	2·3765	31·227	1·56	3·66	0·11	4·51	1·0024	46·65	0·16565	7·815
		2·6427	29·505					1·0027	44·42	0·15773	7·807
Trimethylamine	276·2	1·4924	118·17	1·16	2·90	0·32	3·56	1·0038	19·497	0·07059	0·8002
		1·6010	114·05		2·97	0·30	3·61	1·0041	18·836	0·06820	0·7992
Ethylamine ...	275·5	1·6036	47·789	1·28	3·47	0·14	4·07	1·0038	45·15	0·16388	5·151
		1·9411	43·170					1·0045	41·34	0·15005	5·142
Diethylamine...	265·2	0·8521	50·131	1·09	3·18	0·13	3·58	1·0026	80·97	0·30531	11·44
		0·9696	46·437					1·0029	76·86	0·28982	11·47
Triethylamine..	260·1	1·3864	48·852	1·04	3·06	0·12	3·40	1·0031	51·11	0·19648	6·661
		1·5679	45·675					1·0035	48·37	0·18595	6·660
Propylamine ...	269·3	1·7675	50·472	1·09	3·24	0·14	3·65	1·0051	38·87	0·14432	4·302
		2·0837	46·232					1·0060	36·03	0·13380	4·306
Dipropylamine	257·5	0·9453	52·162	1·01	3·00	0·13	3·32	1·0030	70·18	0·27258	9·655
		1·0615	48·806					1·0034	66·85	0·25961	9·663

Conductivity of carbon dioxide in water in contact with air (Kohlrausch and Maltby, *Wiss. Abhandl. der Reichsanstalt*, 1910, **3**, 210):

at 18·00° = $0·6 \times 10^{-6}$
,, 25·00 = $0·71 \times 10^{-6}$
,, 32·35 = $0·82 \times 10^{-6}$.

First dissociation constant of carbonic acid $= 3·04 \times 10^{-7}$ (Walker and Cormack, Trans., 1900, **77**, 5). Second dissociation constant of carbonic acid $= 0·6 \times 10^{-10}$ (M'Coy, *Amer. Chem. J.*, 1903, **29**, 437). These are the only measurements which have been made, and both refer to 18°. No temperature-coefficients are given. It has to be assumed, therefore, that the ratio of the constants does not change at 25° and 32·35° beyond the wide limits allowable for the determination of a small correction.

The ionic conductivities for the carbonate, hydrogen carbonate, and hydroxyl ions are:

	CO_3.	HCO_3.	OH.
18·00°	70	38	174·0
25·00	83	44	195·9
32·35	96	51	218·9

TABLE IX.

Partition-coefficients of Amines.

	18°.		25°.		32·35°.	
	Concentration in aqueous layer in gram-equivalent per litre.	Partition-coefficient.	Concentration in aqueous layer in gram-equivalent per litre.	Partition-coefficient.	Concentration in aqueous layer in gram-equivalent per litre.	Partition-coefficient.
Methylamine *	0·0817	8·496	0·1203	7·965	0·1399	5·99
	0·0809	8·477	0·1312	8·000	0·0959	6·00
Trimethylamine	0·0688	3·297	0·0677	2·291	0·1182	1·815
	0·0791	3·290	0·0641	2·297	0·1248	1·820
Dimethylamine	0·0759	23·28	0·1203	19·013	0·1003	13·38
	0·0975	23·29	0·1010	19·05	0·1043	13·36
Ethylamine	0·0886	26·14	0·0999	19·11	0·1287	14·76
	0·0666	26·04	0·11612	19·16	0·2479	14·79
	0·0756	26·09	0·11592	19·13	—	—
Diethylamine	0·04836	2·143	0·04828	1·596	0·1200	1·093
	0·05033	2·139	0·04155	1·597	0·1104	1·095
Triethylamine	0·01893	0·13063	0·01041	0·09934	0·01324	0·0694
	0·01907	0·13068	0·01306	0·09947	0·01331	0·0693
Propylamine	0·0973	5·434	0·03837	4·470	0·0602	3·311
	0·0928	5·439	0·04300	4·470	0·0578	3·317
Dipropylamine	0·0764	0·1185	0·0722	0·0769	0·01168	0·05802
	0·0794	0·1188	0·0681	0·0771	0·1199	0·05795
Tripropylamine	0·0003	0·003 (approx.)	—	—	—	—
Ammonia *	0·07709	27·42	0·1498	24·23	0·0999	21·20
	0·11989	27·44	0·1691	24·25	0·2420	21·17
	—	—	0·1987	24·26	—	—

* Partition-coefficient between chloroform and water in these cases.

Summary of Part I.

Complete data have been obtained for the calculation of the relative hydration and ionisation of nine amines in aqueous solution.

(1) The molecular conductivities of nine amine hydrochlorides have been determined with much greater accuracy than is usual with such measurements.

(2) A new formula connecting temperature and conductivity has been proposed, and from it a very important alteration has been suggested for the conductivities of the "standard" ions potassium and chlorine at temperatures above 18°.

(3) The ionic conductivities of nine ammonium ions have been found at three temperatures, and the temperature-coefficients calculated.

(4) Cases of maximum ionisation, which are not accompanied by a maximum in the conductivity temperature curve, have been discovered.

(5) The apparent dissociation constants of nine amines at three different temperatures have been measured with a greater accuracy than has been attempted before.

(6) A method of applying to the measurement of the conductivity of a base, complete corrections for the impurities present in the water has been described.

(7) Accurate measurements of the partition-coefficients of nine amines between water and toluene (or chloroform) have been made at three temperatures.

PART II.

The three temperatures chosen for the measurements of the apparent ionisation constants and partition-coefficients—18°, 25°, and 32·35°—are such that in the notation of the previous paper:

$$\frac{t_2 - t_1}{(273 + t_1)(273 + t_2)} = \frac{t_3 - t_2}{(273 + t_2)(273 + t_3)};$$

thus if q, the molar heat of ionisation, remains constant over the whole range of temperature, the relation $\frac{k''_1}{k'_1} = \frac{k'''_1}{k''_1} = l$ * is strictly true, and the approximation used on p. 1375 of the previous paper becomes unnecessary; the same applies to the relations

$$\frac{k''_2}{k'_2} = \frac{k'''_2}{k''_2} = \frac{1}{m} \quad \text{and} \quad \frac{M''}{M'} = \frac{M'''}{M''} = n.$$

It was expected that the elimination of this approximation, result-

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* Throughout this paper the symbols have the same meaning and the equations the same numbers as in the previous paper (Trans., 1907, **91**, 1373).

ing in greater accuracy in the values of l, m, and n, would bring the values of $\frac{s_1}{r_1}$ and $\frac{s_2}{r_2}$ (which, since $\frac{s_1}{r_1}=\frac{mn}{l}=\frac{s_2}{r_2}$, should be identical) into agreement within the limits of experimental error in every case. Now the errors in the mean values of the ionisation constants and partition-coefficients appear to be seldom greater than 1 in 500, and are often less. Assuming a possible error of 1 in 500 on each side in these quantities, the maximum error possible in $\frac{s}{r}$ is 1 in 125, and could only occur in consequence of a very unlikely distribution of errors in the experimental results. The difference between $\frac{s_1}{r_1}$ and $\frac{s_2}{r_2}$, however, is in every case greater than 1 in 125, and is generally much greater. We are thus led to the conclusion that the values of l, m, and n, or some of them, change with the temperature; which means that the heats of ionisation, hydration, and solution, or some of them, change with the temperature.

The original method of calculation, which involves the constancy of l, m, and n, thus breaks down, for there are now more unknown quantities than there are equations, and a solution can only be obtained by making assumptions as to the value of one or more of the unknown quantities.

One assumption, that n is constant and equal to unity (which is really an assumption that the "true" partition-coefficient of NR_3, apart from the hydroxide, $NR_3H{\cdot}OH$, and its ions, does not alter with the temperature), has been made throughout the following work. That the partition-coefficients of substances, the molecular states of which are the same in both solvents, alter very little with temperature is very generally believed, although there does not seem to be any other basis for this belief than the results of Berthelot and Jungfleisch (*Ann. Chim. Phys.*, 1872, [iv], **26**, 396), which are not very extensive, and a statement by Nernst (*Zeitsch. physikal. Chem.*, 1891, **8**, 117) that he has convinced himself that the temperature-coefficient is small. That the assumption that n=unity does not lead to serious errors in the present work is shown by the fact that the variation in the value of y (the concentration of the substance of type $R_3NH{\cdot}OH$) caused by a change of 2 per cent. in n does not in any case exceed 5 per cent., and is thus of the same order as the unavoidable errors of the method.

Assuming now that n is unity, and since there are possibly two values for l—one for the range 18° to 25°, written l_1 below, and one for the range 25° to 32·35°, written l_2 below—and two values for m—written m_1 and m_2 below—the unknown quantities still exceed the equations by one.* We have, however, what is the equivalent of another equation in the value of the heat of neutralisation of the base, which is a function of k_1, k_2, l, and m. Owing to the form of this function it is not possible to write out the new equation, and, combining it with those we have already, to solve the ten equations for the ten unknown quantities, x_1, y_1, x_2, y_2, x_3, y_3, l_1, l_2, m_1, and m_2. The following was the method used.

From the equation $y_2(s_1l_1 - r_1) = a_1 - z_1 - r_1(a_2 - z_2)$ [the new form of equation (18)] obtain a value of y_2 by substituting the values of s_1, r_1, a_1, a_2, z_1, and z_2, calculated as in the previous paper, and a trial value of l_1; from the new form of equation (19):

$$s_2 l_2 \frac{s_1 l_1 - r_1}{s_2 l_2 - r_2} = \frac{a_1 - z_1 - r_1(a_2 - z_2)}{a_2 - z_2 - r_2(a_3 - z_3)},$$

and the same trial value of l_1, get a value for l_2; from these values of l_1, l_2, and y_2 the values of x_1, x_2, x_3, y_1, y_3, m_1, and m_2 may be calculated by means of equations (10), (11), (12), (13), (14), and the new forms of (15), (16), (20*a*), and (20*b*), namely:

$$(15)\ \frac{y_1}{y_2} = s_1 l_1,\ (16)\ \frac{y_2}{y_3} = s_2 l_2,\ \ (20a)\ \ \frac{s_1}{r} = \frac{m_1}{l_1},\ (20b)\ \frac{s_2}{r_2} = \frac{m_2}{l_2}.$$

It is now possible to calculate the values of k_1 and k_2 for the three temperatures from the values of x, y, and z, and to calculate the heats of ionisation and hydration from l_1 and m_1 for the range 18—25°, and from l_2 and m_2 for the range 25—32·35°; from these the heat of neutralisation of a solution of the base of any concentration may be calculated as described in the case of piperidine (Trans., 1907, **91**, 1381). The whole process is repeated until the value for the heat of neutralisation thus calculated agrees with that found by experiment, when we are justified in assuming that the value of l_1 used, and the values of the other quantities to which this value of l_1 leads, are correct.

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* At first sight it would seem that the nine equations of the previous paper become 10 when l, m, and n vary, for equations (20*a*) and (20*b*) are no longer identical and all the other equations remain, although now containing l_1 and l_2, m_1 and m_2, instead of l and m, and somewhat modified in form. On closer inspection, however, it is seen that the essential difference between equations (19) and (22) is that, in the former, no assumption as to the value of m is involved, whilst in the proof of the latter, m has been assumed constant, and that this difference disappears under the new conditions, where no assumption as to the constancy of m can be made. And even if m were supposed to be constant and only l to vary, one of these equations still becomes useless, for equation (19) in its new form cannot be solved alone, but only in conjunction with (20*a*) and (20*b*), which introduces the constancy of m into it, that is, it can only be solved after it has been made to contain the same assumptions as equation (22); it must inevitably give the same values of l and m as equation (22), whether the assumptions made are justified or not; thus, under the new conditions, either (19) or (22) becomes useless.

That this method, which involves only one assumption, namely, that $n = 1$, leads to correct results, is proved in the case of ammonia by the fact that the value of l_1, which gives the correct value for the heat of neutralisation, gives also the correct value for the heat of solution. The method of calculation of the heat of solution is the same as that used previously (Trans., 1907, **91**, 1383). This confirmation is all the more important in that the values of the partial pressure of ammonia above its aqueous solutions used in the calculation of the heat of solution were taken from Perman's numbers, and are quite independent of our experiments.

The first trial value of l_1 was generally found by solving the equations, either on the assumption that l is constant or that m is constant; sometimes solution was possible on both assumptions, in which case the true value of l_1 could easily be judged, but more often only one of the assumptions gave a possible solution. In the cases of methylamine and propylamine the values of the heat of neutralisation calculated on the assumption that l is constant were near enough to the experimental values to make it unnecessary to take further trial values of l_1.

Results.

The values of a (total concentration of amine in aqueous solution) are the concentrations at which the partition-coefficients were determined; the values of c (concentration in non-aqueous layer) have been calculated from a by use of the mean of the values of the partition-coefficients found for that substance and temperature. All concentrations are expressed in mols. per c.c., and thus the values of the ionisation-constants have to be multiplied by 10^5 to bring them to the units in which this constant is sometimes expressed.

The uncertainty in the values of $\frac{s}{r}$ (which form the basis of the calculation), due to experimental errors in our numbers, cannot be greater than 1 in 125, and is not likely to be greater than 1 in 250. The errors given for l in the following pages are the means of the least and greatest errors produced in l by an error of 1 in 250 each way in the value of $\frac{s}{r}$. No attempt has been made to evaluate the errors in l caused by errors in the heat of neutralisation, since the latter are unknown. It seems likely that the error from this source is greater than that from our measurements.

Ammonia: $\frac{s_1}{r_1} = 1{\cdot}076$; $\frac{s_2}{r_2} = 1{\cdot}095$.

$l_1 = 1{\cdot}160$, $m_1 = 1{\cdot}248$, $l_2 = 1{\cdot}206$, $m_2 = 1{\cdot}320$.

	$c \times 10^5$.	$a \times 10^5$.	$x \times 10^5$.	$y \times 10^5$.	$z \times 10^5$.	$k_1 \times 10^7$.	k_2.
18°	0·4370	11·99	4·92	6·92	0·143	0·294	1·41
25°	0·6182	14·98	6·97	7·85	0·164	0·341	1·13
32·35° ...	0·4712	9·99	5·31	4·53	0·136	0·411	0·85

$NH_3 + H_2O = NH_4OH + 5450$ cals. (For range 18—25°.)
$NH_4OH = NH^{\cdot}_4 + OH' - 3650$,, ,, ,,

Heat of neutralisation calculated, 12,320 cals. (0·278*N*-solution at 18°).

Heat of neutralisation found by Thomsen, 12,250 cals. (0·278*N*-solution at 17·5°).

Heat of solution of ammonia (apart from heat of hydration and ionisation), 5290 cals.

Heat of solution calculated, 8460 cals. (0·3*N*-solution at 18°).

,, ,, found by Thomsen, 8440 cals. (0·3*N*-solution at 20°).

Likely error in l about 1 per cent.
,, ,, ,, k_1 ,, 5 ,, ,,
,, ,, ,, k_2 ,, 10 ,, ,,

Methylamine: $\frac{s_1}{r_1} = 1{\cdot}018$; $\frac{s_2}{r_2} = 1{\cdot}311$.

$l_1 = l_2 = 1{\cdot}034$, $m_1 = 1{\cdot}053$, $m_2 = 1{\cdot}355$.

	$c \times 10^5$.	$a \times 10^5$.	$x \times 10^5$.	$y \times 10^5$.	$z \times 10^5$.	$k_1 \times 10^7$.	k_2.
18°	0·963	8·17	0·441	7·14	0·590	4·87	16·2
25°	1·507	12·03	0·690	10·61	0·731	5·04	15·3
32·35° ...	2·336	13·99	1·069	12·13	0·795	5·21	11·3

$CH_3{\cdot}NH_2 + H_2O = CH_3{\cdot}NH_3OH + 1270$ cals. (18—25°.)
$CH_3{\cdot}NH_3OH = CH_3{\cdot}NH^{\cdot}_3 + OH' - 822$,, ,,

Heat of neutralisation calculated, 12,980 cals. (0·278*N*-solution at 18°).

Heat of neutralisation found by Thomsen, 13,120 cals. (0·278*N*-solution at 17·5°).

Likely error in l_1 about 0·5 per cent.
,, ,, ,, k_1 ,, 10 ,,
,, ,, ,, k_2 ,, 70 ,,

Dimethylamine: $\frac{s_1}{r_1} = 1\cdot153$; $\frac{s_2}{r_2} = 1\cdot176$.

$l_1 = 1\cdot43,\ m_1 = 1\cdot649,\ l_2 = 5\cdot86,\ m_2 = 6\cdot89.$

	$c \times 10^5$.	$a \times 10^5$.	$x \times 10^5$.	$y \times 10^5$.	$z \times 10^5$.	$k_1 \times 10^7$.	k_2.
18°	0·3260	7·59	3·97	2·97	0·650	14·21	0·75
25°	0·6322	12·03	7·69	3·50	0·843	20·32	0·46
32·35° ...	0·7502	10·03	9·12	0·060	0·847	120·2	0·007

$$CH_3\cdot NH_2 + H_2O = CH_3\cdot NH\cdot OH + 12{,}290 \text{ cals.} \quad (18\text{—}25^\circ.)$$
$$CH_3\cdot NH\cdot OH = (CH_3)_2NH^{\cdot} + OH' - 8790 \quad ,, \qquad ,,$$

Heat of neutralisation calculated, 12,000 cals. (0·278*N*-solution at 18°).

Heat of neutralisation found by Thomsen, 11,810 cals. (0·278*N*-solution at 17·5°).

The errors here are possibly very large. The highest value of l_1 that gives real value for x and y is 1·0438, and this therefore gives the lowest value of the heat of neutralisation that agrees with our experimental results, namely, 12,000 cals. The difference between this and Thomsen's value is not large, but in this particular case it happens that the change in l_1 necessary to produce a change of 200 cals. in the heat of neutralisation is very large; thus when $l = 1\cdot10$, the calculated heat of neutralisation is 12,600 cals., and the rate of variation of this quantity with l_1 becomes smaller as l increases.

Trimethylamine: $\frac{s_1}{r_1} = 1\cdot206$; $\frac{s_2}{r_2} = 1\cdot016$.

$l_1 = 1\cdot397,\ m_1 = 1\cdot684,\ l_2 = 1\cdot442,\ m_2 = 1\cdot465.$

	$c \times 10^5$.	$a \times 10^5$.	$x \times 10^5$.	$y \times 10^5$.	$z \times 10^5$.	$k_1 \times 10^7$.	k_2.
18°	2·089	6·88	1·66	5·03	0·190	0·720	3·03
25°	2·951	6·77	2·34	4·22	0 206	1 01	1·80
32·35°	6·505	11·82	5·17	6·35	0·304	1·45	1·25

$$(CH_3)_2N_3^{\cdot} + H_2O = (CH_3)_3NH\cdot OH + 12{,}820 \text{ cals.} \quad (18\text{—}25^\circ.)$$
$$(CH_3)_3NH\cdot OH = (CH_3)_3NH^{\cdot} + OH' - 8220 \quad ,, \qquad ,,$$

Heat of neutralisation calculated, 8,730 cals. (0·278*N*-solution at 18°).

Heat of neutralisation found by Thomsen, 8740 cals. (0·278*N*-solution at 17·5°).

Likely error in l_1 about 0·4 per cent.
,, ,, ,, k_1 ,, 0·7 ,, ,,
,, ,, ,, k_2 ,, 1·5 ,, ,,

Ethylamine : $\frac{s_1}{r_1} = 1{\cdot}366$; $\frac{s_2}{r_2} = 1{\cdot}296$.

$l_1 = 1{\cdot}107,\ m_1 = 1{\cdot}512,\ l_2 = 1{\cdot}128,\ m_2 = 1{\cdot}462.$

	$c \times 10^5$.	$a \times 10^5$.	$x \times 10^5$.	$y \times 10^5$.	$z \times 10^5$.	$k_1 \times 10^7$.	k_2.
18°	0·3389	8·860	1·82	6·38	0·655	6·73	3·50
25°	0·5228	9·990	2·81	6·49	0·695	7·44	2·31
32·35° ...	0·8720	12·870	4·68	7·41	0·789	8·40	1·58

$C_2H_5{\cdot}NH_2 + H_2O = C_2H_5{\cdot}NH_3{\cdot}OH + 10{,}160$ cals. (18—25°.)
$C_2H_5{\cdot}NH_3{\cdot}OH = C_2H_5{\cdot}NH^{\cdot}_3 + OH' - 2500$,, ,,

Heat of neutralisation calculated, 13,470 cals. (0·278*N*-solution at 18°).

Heat of neutralisation found by Thomsen, 13,440 cals. (0·278*N*-solution at 17·5°).

Likely error in l_1 about 2 per cent.
,, ,, ,, k_1 ,, 5 ,, ,,
,, ,, ,, k_2 ,, 15 ,, ,,

Diethylamine : $\frac{s_1}{r_1} = 1{\cdot}258$; $\frac{s_2}{r_2} = 1{\cdot}374$.

$l_1 = 1{\cdot}073,\ l_2 = 1{\cdot}009.$

In this case the minimum value for l_1 to get real values of x and y is 1·073, and this gives the maximum value of the heat of neutralisation compatible with our experimental results, namely, 12,050 cals. (strength of solution 0·5*N*, temperature 15°). Berthelot finds 12,400 cals. at this strength of solution and temperature. This value of l_1, which is the nearest we can get to the truth, gives the concentration of x as zero; that is, we must conclude that the concentration of diethylamine as such is vanishingly small, and that the diethylamine is present almost entirely as diethylammonium hydroxide and its ions. This means that the hydration constant is very large, and the apparent ionisation-constants (the values of which are given below) are in this case the true ionisation-constants:

	$k_1 \times 10^7$.		$k \times 10^7$.		$k_1 \times 10^7$.
18°	10·59	25°	11·36	32·35°	11·46

$(C_2H_5)_2NH_2{\cdot}OH = (C_2H_5)_2NH^{\cdot}_2 + OH' - 1730$ cals. (18—25°.)

Triethylamine: $\frac{s_1}{r_1} = 1{\cdot}201$; $\frac{s_2}{r_2} = 1{\cdot}284$.

$l_1 = 1{\cdot}432,\ m_1 = 1{\cdot}720,\ l_2 = 1{\cdot}912,\ m_2 = 2{\cdot}455.$

	$c \times 10^4$.	$a \times 10^5$.	$x \times 10^5$.	$y \times 10^5$.	$z \times 10^5$.	$k_1 \times 10^7$.	k_2.
18°	1·449	1·893	0·555	1·050	0·287	7·87	1·89
25°	1·313	1·306	0·503	0·553	0·250	11·26	1·10
32·35° ...	1·908	1·324	0·731	0·327	0·266	21·53	0·45

$(C_2H_5)_3N + H_2O = (C_2H_5)_3NH{\cdot}OH + 13{,}340$ cals. (18—25°.)
$(C_2H_5)_3NH{\cdot}OH = (C_2H_5)_3NH^{\cdot} + OH' - 8830$,, ,,

Heat of neutralisation calculated, 9620 cals. (0·5*N*-solution at 18°).

Heat of neutralisation found by Berthelot, 9640 cals. (0·5*N*-solution at 15°).

Likely error in l_1 about 0·5 per cent.
,, ,, ,, k_1 ,, 2 ,, ,,
,, ,, ,, k_2 ,, 6 ,, ,,

Propylamine: $\frac{s_1}{r_1} = 1{\cdot}258$; $\frac{s_2}{r_2} = 1{\cdot}346$.

$l_1 = l_2 = 1{\cdot}020,\ m_1 = 1{\cdot}283,\ m_2 = 1{\cdot}373.$

	$c \times 10^5$.	$a \times 10^5$.	$x \times 10^5$.	$y \times 10^5$.	$z \times 10^5$.	$k_1 \times 10^7$.	k_2.
18°	1·791	9·730	0·628	8·47	0·630	4·68	13·5
25°	0·962	4·300	0·338	3·55	0·412	4·77	10·5
32·35°	1·743	5·780	0·612	4·69	0·478	4·87	7·7

$C_3H_7{\cdot}NH_2 + H_2O = C_3H_7{\cdot}NH_3{\cdot}OH + 6120$ cals. (18—25°.)
$C_3H_7{\cdot}NH_3{\cdot}OH = C_3H_7{\cdot}NH^{\cdot}_3 + OH' - 480$,, ,,

Heat of neutralisation calculated, 13,700 cals. (0·5*N*-solution at 18°).

Heat of neutralisation found by Berthelot, 13,850 cals. (0·5*N*-solution at 15°).

Likely error in l_1 about 0·5 per cent.
,, ,, ,, k_1 ,, 2·5 ,, ,,
,, ,, ,, k_2 ,, 20·0 ,, ,,

Dipropylamine: $\frac{s_1}{r_1} = 1{\cdot}494$; $\frac{s_2}{r_2} = 1{\cdot}272$.

$l_1 = 1{\cdot}036,\ l_2 = 1{\cdot}018.$

The conditions here are exactly similar to those described in the case of diethylamine. The minimum value of l_1 possible—1·036—gives 12,900 cals. as the heat of neutralisation of a 0·5*N*-solution at 18°, and this is the maximum value compatible with our experimental results; Berthelot finds 13,450 cals. for a 0·5*N*-solution at

15°. In this case, as for diethylamine, we must conclude that the hydration constant is very large, and that the "true" and "apparent" ionisation-constants coincide in value:

$k_1 \times 10^7$............ 9·157 9·488 9·659

$$(C_3H_7)_2NH{\cdot}OH = (C_3H_7)_2NH^{\cdot} + OH' - 870 \text{ cals.} \quad (18\text{—}25°.)$$

Collected Results.

	$k_1 \times 10^7$.			k_2.			Heat of ionisation.	Heat of hydration.
	18°.	25°.	32·35°.	18°.	25°.	32·35°.		
Ammonia	0·294	0·341	0·411	1·41	1·13	0·85	−3650	5450
Methylamine ...	4·87	5·04	5·21	16·2	15·3	11·3	− 820	1270
Dimethylamine	14·21	20·32	(120·2)	0·75	0·46	(0·007)	−8790	12290
Trimethylamine	0·720	1·01	1·45	3·03	1·80	1·23	−8220	12820
Ethylamine ...	6·73	7·44	8·40	3·50	2·31	1·58	−2500	10160
Diethylamine...	10·59	11·36	11·46	large	large	large	−1730	—
Triethylamine..	7·87	11·26	21·53	1·89	1·10	0·45	−8830	13340
Propylamine ...	4·68	4·77	4·87	13·5	10·5	7·7	− 480	6120
Dipropylamine	9·16	9·49	9·66	large	large	large	− 870	—

No simple relations between the values of the constants and the chemical constitution of the substances appear from this table. Taking the constants at 18°, we see that ammonia has the smallest and diethylamine the largest ionisation-constant, the ratio between the two being 48; the methylamines, ethylamines, and propylamines all agree in showing an increase in the ionisation-constant from the primary to the secondary compound, and the methylamines and ethylamines both show a decrease from the secondary to the tertiary compounds, although the relation is altered at 32·35° for the ethylamines, where the tertiary compound has the larger value of k_1. Comparing isomerides—ethylamine with dimethylamine, and dipropylamine with triethylamine—we see that the secondary amines have larger values for k_1 than the primary and tertiary.

With regard to the variation of k_2 with constitution, even less can be said. Of the three primary amines one has a small hydration-constant and two have large ones; of the three secondary amines one has a small hydration-constant and two very large ones; and both the tertiary amines have small hydration-constants.

Irregularities of the kind found in the above table are also observed in the effects of substitution of alkyl groups in aliphatic acids on their ionisation-constants. It appears that the specific effects of the alkyl groups on the ionisation-constant, due to their slightly electropositive nature, are masked by stereochemical effects (Moore, Lehfeldt's "Electrochemistry," p. 119; Flürscheim, Trans., 1909, **95**, 718), and probably also by the effect of an alteration in the distribution of affinity in the molecule (Flürscheim, *loc. cit.*).

In the paper quoted, Flürscheim attempted to evaluate the relative magnitudes of these effects for a number of atoms and radicles, and the application of his results showed that they are capable of explaining to a very large extent the variation in the ionisation-constants actually found by experiment, although some anomalies remain (for example, trimethylacetic acid). It must be borne in mind that the steric effect, and the effect on the distribution of affinity, of the substitution of any particular radicle, must depend to a very large and at present indeterminate extent on the nature of the whole molecule undergoing the reaction, on the temperature, and possibly on other conditions; for these reasons Flürscheim's numbers must be regarded as tentative.

With regard to amines, Flürscheim states that there is no reason to suppose that the intermediate form, $RNH_3{\cdot}OH$, in the equation

$$R{\cdot}NH_2 + H_2O \qquad R{\cdot}NH_3{\cdot}OH \rightleftharpoons R{\cdot}NH^{\cdot}_3 + OH'$$

has any real existence, and writes the equation as:

$$R{\cdot}NH_2 + (H \;.\;.\;.\;.\; \oplus) \rightleftharpoons (R{\cdot}NH_3 \;.\;.\;.\;.\; \oplus).$$

If this were true then for all amines and all temperatures, both y and k_2 would be zero, and the calculations in this paper would have given values approximating to these. Since the actual results are so different, we must conclude that the amine hydroxides have a real existence, so that Flürscheim's discussion of the variation of the ionisation-constants of the amines with constitution has little value.

The most interesting question arising out of the results of this paper is the relation between the quaternary hydroxides, such as tetraethylammonium hydroxide, and the hydrates of the amines. The ionisation constants are:

	18°.		18°.
$CH_3{\cdot}NH_3{\cdot}OH$	$4{\cdot}87 \times 10^{-7}$	$C_2H_5{\cdot}NH_3{\cdot}OH$	$6{\cdot}73 \times 10^{-7}$
$(CH_3)_2NH_2{\cdot}OH$	$14{\cdot}21 \times 10^{-7}$	$(C_2H_5)_2NH_2{\cdot}OH$	$10{\cdot}59 \times 10^{-7}$
$(CH_3)_3NH{\cdot}OH$	$0{\cdot}72 \times 10^{-7}$	$(C_2H_5)_3NH{\cdot}OH$.........	$7{\cdot}87 \times 10^{-7}$
$(CH_3)_4N{\cdot}OH$	(Very strong base).	$(C_2H_5)_4N{\cdot}OH$............	(Very strong base).

It does not seem possible that the small changes among the first three members of each group, and the enormous changes from the third to the fourth members, can be due to the same influences. We must assume that there is a definite change of constitution, that is, that the forces joining the molecule together are altered very considerably either in strength or direction, or both, when the last hydrogen atom is replaced by an alkyl group.

Werner ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," p. 101; *Ber.*, 1903, **36**, 152) applies his theory of co-ordination to these compounds, the ammonium chlorides and hydroxides being supposed to be derived from hydrochloric acid and alkyl chloride, and water and alkyl hydroxide, the hydrogen and alkyl groups of which are supposed to have unity for their co-ordination numbers. The formulæ of the various compounds become:

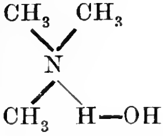
Ammonium chloride	$(NH_3 \ldots\ldots\ldots H)Cl$
Ammonium hydroxide	$(NH_3 \ldots\ldots\ldots H)OH$
Methylamine chloride	$(CH_3 \cdot NH_2 \ldots\ldots H)Cl$
Methylamine hydroxide	$(CH_3 \cdot NH_2 \ldots\ldots H)OH$
Tetramethylammonium chloride	$(N(CH_3)_3 \ldots\ldots CH_3)Cl$
Tetramethylammonium hydroxide.	$(N(CH_3)_3 \ldots\ldots CH_3)OH$.

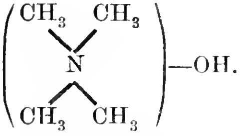
Thus on Werner's theory ammonium chloride is hydrochloric acid in which the hydrogen atom has become attached to a molecule of ammonia, the chlorine atom maintaining much the same relation to the hydrogen atom as in the original molecule of hydrochloric acid; for this reason the degrees of ionisation of ammonium chloride and hydrochloric acid are practically the same, and for a similar reason, ammonium and amine hydroxides, derived from the very weak electrolyte water, are themselves very weak electrolytes. Admirable as this theory seems as applied to ammonia and the primary, secondary, and tertiary amines, in which the co-ordinating valency of hydrogen is exerted, it breaks down when applied to the quaternary compounds, where it leads to the conclusion that the ionisation of tetramethylammonium chloride will be of the same order of magnitude as that of methyl chloride, and that the ionisation of tetramethylammonium hydroxide will be of the same order of magnitude as that of methyl alcohol.

Meisenheimer (*Ber.*, 1909, **41**, 3966), although accepting Werner's view that the negative group is not directly attached to nitrogen in the quaternary compounds, supposes that whilst the four positive groups arrange themselves at the corners of a tetrahedron, the centre of which is occupied by the nitrogen atom, the negative group takes up a position on one of the faces, thus differing from Werner, who supposes the negative atom or group to remain permanently under the influence of the positive atom or group with which it was originally combined. It appears to the author that the following combination of the views of Werner, Meisenheimer, and Flürscheim is capable of explaining most, if not all, of the experimental facts.

Accepting Werner's view for the hydroxides and chlorides of primary, secondary, and tertiary amines, that is, supposing that there is no direct union between the negative group and nitrogen, and that the former is always mainly influenced by the hydrogen to which it was originally attached, we see some reason for the absence of definite relations between changes of constitution of the amines and the ionisation constants of their hydroxides. For this change of constitution does not affect the hydroxyl group directly (or only to a very limited extent), but through the hydrogen atom, and the strength of the union between the amine molecule and the hydrogen atom is not improbably a highly constitutive property affected largely by steric influences. Some justification for supposing that the negative group remains practically entirely under the influence of the hydrogen atom with which it was originally combined is obtained by the application of Flürscheim's idea of the distribution of affinity in the molecule; for the unions between the alkyl groups and nitrogen in the amine being very strong, there can be but little residual affinity left in the amine molecule, and this is used in joining the amine to the hydrogen, so that the amine will have little or no force with which to act directly on the negative group. A further application of the same idea gives some explanation of the magnitudes of the ionisation-constants of the amine hydroxides, for the union between the amine and the hydrogen atom of the water being weak, the latter will still be able to exert a great deal, although not all, of its affinity on the hydroxyl group; thus the ionisation-constants of the amine hydroxides should all be small, although greater than that of water. But when we come to a quaternary compound such as tetramethylammonium hydroxide, that is, as soon as there is no hydrogen directly attached to nitrogen, the conditions become very different. The methyl group to which we may suppose that the hydroxyl was originally attached is now joined to the nitrogen by a very strong union, and thus has practically no affinity left with which to attract the hydroxyl group, which therefore is split off easily as an ion; and since the residual affinities of all four methyl groups must be the same, no particular one of them can exert a special influence on the hydroxyl group, which in the non-ionised compound will probably take up a position on one of the faces of the tetrahedron as supposed by Meisenheimer. Whether the nitrogen atom has any affinity left with which to attract the hydroxyl group, or whether the nitrogen atom is completely satisfied and the residual affinity is with the methyl groups, it is, of course, impossible to say. In either case the force on the hydroxyl group must be very weak. If the four alkyl groups are not identical, the relations will remain unaltered, except that the hydroxyl group must now come to rest on one particular face of the tetrahedron, whereas in the symmetrical compound it could occupy any face.

The following formulæ, where thick strokes mean strong unions and thin strokes weak unions, show roughly the difference between trimethylammonium hydroxide and tetramethylammonium hydroxide:


Weak electrolyte.


Strong electrolyte.

Briefly, the author accepts Werner's view for the unstable ammonium hydroxides, in which there is at least one hydrogen atom attached to the nitrogen, and Meisenheimer's view for quaternary hydroxides and chlorides, the transition from one type to the other and the difference in properties between the two types being explained by Flürscheim's theory of the distribution of affinity in the molecule. Ammonium hydroxide is a special case, and might belong to either type equally well; if it belongs to the second type it would have its hydroxyl attached firmly to nitrogen, which, since the hydrogen atoms are not joined to it by strong unions, would have considerable residual affinity.

It is necessary to point out that the values of the hydration-constants (k_2) given in this paper do not support the view. Since k_2 is a measure of the affinity between the amine and water, the theory described above demands that k_1 and k_2 should increase and decrease together, while, in fact, there is no such relation. This discrepancy loses some of its weight when it is remembered (1) that the errors in the values of the hydration-constants may be large, being possibly 70 per cent. in the case of methylamine, and not improbably larger in the case of the three secondary amines; and (2) that this relation between k_1 and k_2 can be predicted only if the alkyl groups in the amine molecule have no specific effect on its ionisation-constant, whilst as a matter of fact there is no reason to doubt that such specific effects exist, although one cannot estimate their magnitude.

The advantages of the author's theory * are (1) that it is in agree-

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* It seems to the author not unlikely that the mechanism of ionisation in general may involve processes similar to those considered here. It is well known that most, if not all, ions in aqueous solution exist in combination with water. If in sodium chloride, for example, both the sodium and chlorine exert a great deal of their combining power on molecules of water, there will be little force left to keep them in combination, and if other circumstances are favourable, ionisation will take place. The difference, as regards power of ionisation, between inorganic and organic acids may be explained at once on this idea, for presumably the organic anions will have much less affinity for water than the inorganic anions; and the increase in the ionisation-constant of an organic acid by the substitution in it of an atom or group

ment with Werner's general theory of ammonium compounds, for which there is a great deal of evidence (Werner, *loc. cit.*); (2) that it is in agreement with Meisenheimer's work on optically active amine oxides, and generally with the work on the stereoisomerism of the quaternary nitrogen compounds; (3) that it explains for the quaternary alkyl compounds of phosphorus, arsenic, antimony, sulphur, and tellurium in the same way as for the quaternary nitrogen compounds the properties which distinguish them so sharply from the corresponding primary, secondary, and tertiary compounds, and at the same time explains why the trimethylstannic hydroxide, although of the same type as the above-mentioned highly ionised compounds, is a weak base; for the alkyl groups are known to be much less firmly attached to tin than to the above-mentioned elements, and the tin has thus more affinity with which to bind the hydroxyl group.

Summary of Part II.

(1) The method already proposed by Moore for the calculation of the ionisation and hydration constants of amines has been modified to meet new conditions.

(2) The modified method has been applied to ammonia, the methylamines, ethylamines, and the primary and secondary propylamines.

(3) A general theory of the primary, secondary, tertiary, and quaternary compounds of nitrogen, applicable to similar compounds of phosphorus, arsenic, antimony, sulphur, tellurium, and tin has been proposed.

The authors wish to express their thanks to the Government Grant Committee and to the Chemical Society for grants which have defrayed part of the expense of this investigation.

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(for example, chlorine), which when itself combined with hydrogen gives a strong acid, and which therefore on this theory has a strong affinity for water, may be due to the increased power of the anion of using up its affinity in combining with water.

Al Prof. William A. Tilden
Roma il 13 Aprile 1898
S Cannizzaro

To face p. 1677.

CANNIZZARO MEMORIAL LECTURE.

Delivered on June 26th, 1912,

By Sir William A. Tilden, D.Sc., LL.D., F.R.S., Past-President of the Chemical Society.

The minutes of the Ordinary Scientific Meeting of the Chemical Society for June 19th, 1862, contain the following entry: "Messrs. Cannizzaro, Kekulé, Löwig, Malaguti, Marignac, Pasteur, Stas, and Zinin were elected Foreign Members."

Of this illustrious band not one now remains,* and the Society having paid its tribute to each in turn is gathered on this occasion to commemorate the name which, of those enumerated, was the last to disappear from its roll of Honorary Members.

The career of Stanislao Cannizzaro was completed in an age and country full of romance. Born as he was under the reign of a Bourbon in the kingdom of the two Sicilies, he lived to see the miserable conditions which beggared and enslaved his own compatriots swept away; he took a part as soldier and Senator in the regeneration of Italian nationality, and during the latter half of his long life he enjoyed the freedom which belongs to a united people under a constitutional Monarchy.

His experiences as a man of science were no less remarkable, for it may be said he began work almost before modern chemistry, of which he helped to lay the foundations, had been called into existence. When Cannizzaro was twenty years of age, Liebig in Germany, and Dumas in France were at the height of their fame; while in England Williamson's ideas were beginning to attract serious attention. Many years had yet to elapse before a real system could be applied to the masses of facts then so rapidly accumulating.

Stanislao Cannizzaro was born in Palermo on July 13th, 1826.† The family came from Messina, and its members at different times held important offices in that city and elsewhere in Sicily. Stanislao's father, Mariano Cannizzaro, was born in Messina, but he became a magistrate in Palermo and Minister of Police, and later President of the Gran Corte dei Conti. The mother was Anna di Benedetto, a member of a noble Sicilian house. There was a large family, of which Stanislao was the youngest. He was educated

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* Kekulé died in 1896, Löwig in 1890, Malaguti in 1878, Marignac in 1894, Pasteur in 1895, Stas in 1891, and Zinin in 1880.

† For the facts relating to his father's life, I am indebted chiefly to Mr. Mariano Cannizzaro.

partly at the Reale Collegio Calasanzio, where he won prizes, with distinction especially in mathematics. As may be imagined, the school curriculum in Sicily, as in the whole of Southern Italy, in Cannizzaro's youth was entirely under the control of the priests. Education, "frowned on as a design of the Liberals to revolutionise the State, was so successfully discouraged that in 1837 it was calculated that 2 per cent. of the rural population could read, and not very much more of the dwellers in the towns." * The subjects were confined to the classical languages, grammar, and rhetoric, with a little mathematics.

In 1841, at the age of fifteen, Cannizzaro began the study of medicine at the University of Palermo, and especially the study of physiology under Professor Foderà. The University was at that time in a very imperfect condition, degrees being conferred only in the faculties of medicine, law, and theology. Cannizzaro took no degree, but in 1845 proceeded to Naples, where his sister Angelina had married the Marquis Ruffo, son of King Ferdinand's Prime Minister. Here, after taking part in the proceedings of the physiological section of the scientific congress held in that year, he made the acquaintance of the famous physicist Melloni, and after working for a short time in his laboratory he proceeded, with a warm recommendation from Melloni, to Professor Piria at Pisa. The influence of Piria over his young assistant was fortunately sufficient to determine the latter to devote himself permanently to chemistry. Piria was just then at the height of his fame, justly following his discovery of the constitution of salicin, a very noteworthy feat in those early days of organic chemistry.

Cannizzaro, although an enthusiastic student, could not escape the effects of the political agitation which exercised an influence so powerful on his compatriots at that time. Those were dark days in the history of the country, and the atrocities committed in the name of order by Ferdinand's government had aroused not only the spirit of the Sicilians, but the indignation of, at least, the English people. Beside, Italian soil was occupied in the north by the armies of Austria, there was clerical misrule in the Papal States, and throughout Europe revolution was the order of the day. Cannizzaro responding to the prevalent feelings of patriotic fervour, joined in the premature rebellion in Sicily. Returning from Pisa to his native country in 1847, he joined the Sicilian artillery, and commanded a battery at Messina. After the fall of Messina he was sent to Taormina with a Government commission to oppose the advance of the Neapolitan troops under the General Principe Filangeri, but after March, 1849, the defeat at Novara, and the

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* Trevelyan's "Garibaldi and the Defence of the Roman Republic," p. 55.

abdication of Charles Albert, the Sicilians were obliged to retreat towards Palermo, Cannizzaro being among the last to oppose the Neapolitans. On the fall of the Sicilian Government he embarked with some others on board the frigate *Independente*, which, escaping the Neapolitan fleet, succeeded in reaching Marseilles. After some months Cannizzaro made his way to Paris, and having found admission, presumably through the introduction of Piria, into the laboratory of Chevreul, he resumed his chemical studies. Here he joined Cloëz in work on cyanogen chloride and the production of cyanamide, and their results, published in 1851, constituted Cannizzaro's first contribution to the records of chemical research (*Compt. rend.*, 1851, **32**, 62).

At the close of 1851 he was able to return to Italy, having been appointed professor at the National School at Alessandria, where he had the advantage of a small laboratory and the services of an assistant, "un farmacista giovane intelligente" (letter to Bertagnini). Here he was so occupied, body and mind, with his teaching that, as he complained to his friend Bertagnini, he had little hope of being able to pursue his own studies. Notwithstanding these unfavourable conditions, however, he discovered in 1853 the alcohol corresponding to benzoic acid, which he obtained by the action of potassium hydroxide on benzaldehyde (*Annalen*, 1853, **88**, 129), and which he continued to study during several succeeding years (*Ann. Chim. Phys.*, 1855, [iii], **43**, 349; *Nuovo Cim.*, 1855, **2**, 212).

The summer holiday of 1852 was spent with Bertagnini, who had a small private laboratory at Montignoso, and here the friends carried out work on anisic alcohol, which, however, was not published until 1856 (*Ann. Chim. Phys.*, 1856, [iii], **47**, 285). In 1854 Piria, in association with Matteucci, produced the first number of the new journal *Il Nuovo Cimento*, which was to be the organ of the Pisan school, and to the second volume Cannizzaro made the contribution referred to above. *Il Nuovo Cimento* was not established without some suspicion on the part of the Censor, the Chancellor Cardinal Archbishop, that chemistry and physics, "scienze pericolose," might cause some damage to the faith (*Nuova Antologia*, June, 1911, 490).

In 1855 Cannizzaro accepted an invitation to the Chair of Chemistry in the University of Genoa, at the same time Piria * being transferred to Turin, while Bertagnini was appointed to replace him at Pisa.

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* That Piria was the founder of the Italian School of Chemistry was attested by Liebig. Piria held Cannizzaro in high esteem, which was repaid by the admiration of the pupil, and expressed many years later in Cannizzaro's "Vita e opere di R. Piria," 1883.

At Genoa there was at first no laboratory, and it was only in the year following his appointment that Cannizzaro could obtain rooms in which to carry on his work.

At this time, or probably earlier, he must have begun to meditate on those fundamental questions in chemical theory which led to the famous "Sunto di un Corso di Filosofia Chimica," communicated, in March, 1858, through Professor di Luca to the *Nuovo Cimento* (**7**, 321). But his philosophical and scientific studies, as well as his teaching, were destined to be once more interrupted by the political events which at this time followed one another so rapidly in Italy. In the spring of 1860, the discontent of Southern Italy, responding to the unhappy events in the North, found vent in the insurrection which broke out in April of that year, although it was crushed almost immediately by the Neapolitan Royalist troops. However, Garibaldi with his famous thousand succeeded in effecting a landing at Marsala, in Sicily, on May 11th, and ultimately forced his way into Palermo. The story has been often told, and is full of the most astounding and romantic incidents.* As soon as Garibaldi had entered Palermo, Cannizzaro started for Sicily with the second expedition under General Medici, although he took no part in any battle. In Palermo he became a member of the Extraordinary Council of State of Sicily.

In October of the following year, 1861, he was called from Genoa to his native town, and was appointed Professor of Chemistry in the University of Palermo. Here, again, he had no laboratory, and it was only in 1863 that provision was made for practical work. His activity extended beyond the duties of the office he held in the University, for beside occupying a position on the Municipal Council he made great efforts to secure the establishment of schools, which were almost entirely wanting, as well as to provide for the higher education of women.† He also established an evening drawing school for workmen, and in this school his only son, then a child, received his first lessons in art. Later he became Rector of the University, and in 1867 he acted as Commissioner of Public Health during one of the severe outbreaks of cholera, in the course of which he lost a sister, struck down by the disease whilst nursing the sick.

Cannizzaro remained in Palermo about ten years, and during this period the work he was able to accomplish in chemical research related chiefly to the derivatives of benzylic alcohol and other aromatic substances. It is interesting to recall in this connection

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* See Trevelyan's "Garibaldi and the Thousand."

† *Nuova Antologia* (June, 1911, 492) gives a full account of his benevolent exertions in this and other directions.

S. CANNIZZARO IN 1858.

From a Portrait by D. Salorson.

To face p. 1680.

the fact that among the young men who came under his influence at that time was one whose name a very few years later became renowned throughout the chemical world on account of the great memoir (1874), in which was established once for all the principle by which the orientation of all the derivatives of the so-called aromatic substances can be determined. Körner's rule is familiar to even junior students of organic chemistry. The names of Körner and Cannizzaro are associated together in the authorship of a paper on anisic alcohol (*Gazzetta*, 1872, **2**, 65).

In 1871 Cannizzaro was called to Rome to occupy in the new University the Chair of Chemistry, which he retained until death summoned him away so many years later. Even in the capital city he again found no laboratory, and he was obliged to suspend his researches whilst occupied in organising the chemical institute which found shelter in the old monastic buildings in the Via Panisperna. Here he ultimately established a school, and in spite of the heavy official duties which devolved on the professor he continued during many years the study of the complex and interesting compound, santonin, and worked out its constitution with the co-operation of his pupils and assistants, Amato, Carnelutti, Gucci, Sestini, Valente, and others.

At the same time that he received the call to the University he was made a Senator of the kingdom, and as a Moderate Liberal played his part in shaping the Constitution, and establishing reform in the affairs of the now united Italy. Among other duties which fell to his lot was the organisation of the Customs laboratory and the State Regia dei Tabacchi. He was also a member of the higher Council of Public Instruction, of which for some time he was President. He further occupied himself with the provision of public instruction in agriculture, and generally in helping forward the advancement of science and of the liberal professions in Italy. When the Congress of Applied Chemistry met in Rome in the year 1906, Cannizzaro was Honorary President, and it was gratifying to the visitors from so many lands to see the vivacity and energy with which the old man, then in his eightieth year, entered into all the proceedings. He was still lecturing, and some of the members had the privilege of hearing him address his class in the lecture room of the Chemical Institute. It was from this room four years later that his remains were borne by a company of his students to their last resting place. We are informed that he continued to lecture until the year before his death: "for him to teach was to live." As soon as he perceived that his strength was failing so much that he could not lecture, all his ailments appeared to increase, and the end soon came. He died on May 10th, 1910.

Cannizzaro married in Florence, in 1856 (or 1857?), an English lady, Henrietta Withers, daughter of the Rev. Edward Withers, who held a living in Berkshire. He left one son, who practices in Rome as an architect, and a daughter.

Active as he was as an investigator in the domain of organic chemistry, Cannizzaro's chief claim to the admiration of his contemporaries and to a distinguished place in the history of modern chemistry is based on the systematic course of theoretical teaching which he sketched in 1858.

To form a just estimate of the influence exercised on the progress of scientific chemistry by Cannizzaro's famous essay, a brief review of the state of knowledge and opinion in the chemical world up to and about the year 1858 is necessary.

The atomic theory of Dalton was just fifty years old, and although well rooted in the literature of chemistry there were not a few who still refused to recognise it, and there were many super-cautious chemists who preferred to speak of it as "at the best but a graceful, ingenious, and in its place useful hypothesis."* Evidence of the persistence of this attitude so late as 1869 is afforded by Williamson's lecture,† and especially by the discussion which ensued upon it. Some thought to perceive a distinction between physical atoms and chemical atoms, but generally they seem to have retained the fundamental notion of Dalton, which conceives each atom to be a sphere existing either alone or in close contiguity with other similar atoms, and separable more or less from one another by the influence of heat. Students at this time were generally unfamiliar with the word "molecule,"‡ for chemists spoke as complacently, and in a sense as justly, about an *atom* of water as about an atom of oxygen. For the most part, also, they had never heard the name of Avogadro. Considerable advances had been made toward the estimation with exactitude of what were then usually, although incorrectly, called "atomic weights," notably by Berzelius, Dumas, Pelouze, de Marignac, and Stas. The figures thus afforded by experiment were only equivalents or combining proportions, uncorrected by reference to any standard, for the excellent reason that there was no standard generally recognised; and even in the use of the term "equivalent" there was the utmost confusion, of which evidence is provided by the statement in one of the most widely circulated text-books of the period (Fownes, 1856) that the

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* "Fownes' Chemistry," 6th ed. (1856), p. 210. Edited by Bence Jones and Hofmann.

† *Journ. Chem. Soc.*, 1869, **22**, 328.

‡ The word *molecule* was occasionally used by Dalton, *e.g.*, "Chemical Philosophy," Vol. I., p. 70, and in the sense of atom by Ampère (*Ann. Chim. Phys.*, 1814, **90**, 43).

numbers called equivalents "represent quantities capable of exactly replacing each other in combination," the list of numbers referred to including nitrogen 14, carbon 6, whilst hydrogen was 1, and all were said to be equivalent to oxygen taken as 8. In the same book the law of Gay-Lussac relating to combination of gases by volume is "explained" by the statement (p. 203) that "quantities by weight of the several gases expressed by their equivalents, or, in other words, quantities by weight which combine, occupy, under similar circumstances of pressure and temperature, either equal volumes or volumes bearing a simple proportion to each other." Examples quoted in connexion with this passage show that the volumes of equivalents of elements and compounds as then recognised varied from $\frac{1}{2}$ vol. for O to 2 volumes for HCl and NH_3.

The consequences of bringing them all to the same volume were at this time, and even much later, not considered by the great majority of teachers, and although vapour densities were frequently the subject of experiment, the results were used merely to check the empirical formula deduced from analysis of the substance, and few thought of adopting a standard volume and revising the empirical formula so as to harmonise with it. If, for example, the vapour density of acetone was found, it would be used merely to substantiate the formula deduced from analysis, namely, C_3H_3O ($C=6$, $O=8$), and "whether the rational formula of acetone is C_3H_3O or $C_6H_6O_2$ or $C_9H_9O_3$, the vapour density does not enable us to decide" (Galloway's "Second Step," 1864, p. 68).

This is surprising in view of the fact that so far back as 1826 Dumas, in the memoir in which he describes his well-known method of taking vapour densities,* refers to the fact that all physicists agree in supposing that in elastic fluids under the same conditions the molecules are placed at equal distances, or in equal numbers in the same volume. The difficulties encountered in the general application of this principle to the determination of formulæ arose chiefly from the lack of trustworthy experimental data. But these were gradually accumulating in the years which followed, and by the time Gerhardt and Laurent began to handle the fundamental propositions relating to theoretical chemistry there was a large body of facts, sufficient as it now appears to have provided safe ground for generalisation.

Up to this time also the conception that the ultimate particles of the elements themselves might contain more than one atom had not been commonly accepted. It was believed that combination could only occur between substances of opposite chemical or electro-

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* "Sur quelques points de la Théorie atomistique" (*Ann. Chim. Phys.*, 1826, **33**, 337).

chemical character, hydrogen with oxygen, for instance, but that hydrogen could unite with hydrogen, or oxygen with oxygen, was not generally admitted.

It is evidence of the complete neglect with which Avogadro's great memoir * of 1811 had been treated that chemists generally at this time did not know or had completely forgotten that the constitution of elementary molecules in the gaseous state had been very clearly explained by him. The passage is rather long for quotation in full, but in the second division of the memoir he discusses the case of the "elementary molecules," and his position is indicated clearly enough by the case of water. He says: "Ainsi la molécule intégrante de l'eau, par exemple, sera composée d'une demi-molécule d'oxigène avec une molécule, ou, ce qui est la même chose, deux demi-molécules d'hydrogène." This view of the constitution of elementary molecules did not, therefore, originate with Gerhardt, to whom the idea is usually attributed.

Gerhardt in 1843 had pointed out that the equivalents accepted for organic compounds did not agree with those assigned to mineral substances, and in order that they might correspond with H_2O, CO_2, and NH_3, the formulæ he assigned to water, carbon dioxide, and ammonia respectively, they required to be reduced to one half. At the end of a series of papers on the subject (*Ann. Chim. Phys.*, 1843, **7**, 129, and **8**, 238) he sums up his conclusions in the following sentences:

"Atomes, équivalents et volumes sont synonymes.

"Les densités des gaz sont proportionelles à leurs équivalents."

The fourth volume of his famous "Traité de Chimie Organique" (1856) contains an exposition of his system, in which the molecule of water is taken as the unit, and is represented by the formula H_2O ($O = 16$). From this he was led to represent elementary hydrogen as hydrogen hydride, HH, and gaseous chlorine as chlorine chloride, ClCl. This conception of the constitution of elementary molecules was not derived from any direct consideration of the views of Avogadro or Ampère, whose names are not mentioned. They arose doubtless from acceptance of the principle already acknowledged by Dumas as the prevailing doctrine among physicists, namely, that equal volumes of gases contain the same number of molecules, but Gerhardt never explicitly accepted this principle as a means of settling molecular magnitudes, nor did he seem to give it a position of prime importance among recognised

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* Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps, et les proportions selon lesquelles elles entrent dans ces combinaisons (*J. de Physique, etc.*, **73**, 58–76. Paris, July, 1811. Translated in No. 4 Alembic Club Reprints. Also reprinted in full by the R. Academy of Sciences, Turin, 1911.)

principles. In his little book * published in 1848 before the issue of his great work on organic chemistry, the following passage occurs (p. 43): "Comme il importe toutefois d'adopter une notation exprimant les plus de faits à la fois, j'ai proposé il y a quelques années, de tenir compte des volumes, et de ramener à un même volume les formules des composés volatils, notamment des composés organiques. . . . Comme OH_2 correspond à 2 volumes j'ecris aussi les corps suivants ainsi: CO, CO_2, NH_3, ClH, NO_2, C_2H_6O, SO_3, etc."

His system of formulæ appears to have been based chiefly on his own view that every chemical change is a form of double decomposition, and he is at great pains to show that in chemical reactions, whether of combination or decomposition, the proportion of water or of carbonic acid involved was never less than the amount represented by the formulæ H_2O and CO_2, in which $H=1$, $O=16$, and $C=12$; and, similarly, the amount of free oxygen or hydrogen was never less than the amount represented by O_2 and H_2 with the values as just stated. In his "Traité" (Vol. IV., p. 568) he distinguished the radical hydrogen from the gas hydrogen, the radical chlorine from free chlorine, and he explains that it is the study of reactions which has led him to write hydrogen gas as made up of the two radicals HH, and chlorine gas as composed of the two radicals ClCl; and he goes on to say: "Dans la nomenclature usuelle le gaz hydrogène serait donc l'hydrure d'hydrogène, et le gaz chlore serait le chlorure de chlore; cela veut dire que le gaz chlore et le gaz hydrogène resultent de doubles décompositions."

This mode of viewing the subject led him into some mistakes, of which an example occurs a few pages further on (p. 571), where he represents the action of hydrochloric acid on zinc by an equation in which the zinc molecule is represented as a double structure like that of hydrogen; thus:

$$ZnZn + ClH = ZnH + ClZn$$

and

$$ZnH + ClH = HH + ClZn.$$

The molecule of mercury is also represented by a corresponding formula, HgHg (p. 575).

As regards the constitution of the molecules of the elements, it should not be forgotten that it was in 1850 that Brodie published his views "on the Condition of Certain Elements at the Moment of Chemical Change" (*Phil. Trans.*, 1850, II, 759, and *Quart. Journ. Chem. Soc.*, 1852, **4**, 194). In this memoir he expresses the opinion "that at the moment of chemical change the same chemical relation exists between the particles of which certain elements consist, as between the particles of compound substances under similar cir-

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* Introduction à l'étude de la Chimie par le système unitaire, 1848.

cumstances, on which relation the phenomena of combination depend; that, in short (to use the common language), the particles of the elements have a chemical affinity for each other"; and then he goes on to suggest that the term *affinity*, which is unsatisfactory, should be replaced by the term "polar relation," which serves to indicate an analogous condition "between a series of particles undergoing chemical change and a series of particles conducting electricity or magnetism." These views are illustrated by reference, *inter alia*, to the decomposition of oxide of silver by hydrogen peroxide, previously observed by Thénard, and the mutual interaction of cuprous hydride discovered by Wurtz with hydrochloric acid. The former of these two changes results in the evolution of oxygen gas, and the latter in the production of hydrogen gas, and they were explained by Brodie on the assumption of opposite polar relations in the atoms which combined together in pairs

Gerhardt's system of four types—water, hydrochloric acid, ammonia, and hydrogen—was adopted by him only for the purpose of classifying reactions, as he insisted repeatedly that any knowledge of the arrangement of atoms in a compound is inaccessible to experiment. Dumas' earlier theory of types had implied the idea of arrangement in the constituent parts of bodies, and, indeed, the existence of transferable radicals, or residues as they were called by Gerhardt, such as cyanogen, benzoyl, and ammonium, involved some notion of order within the ultimate particle.

At the time under review the conflict between the notation in equivalents and the notation corresponding to Gerhardt's types had not been decided. The notation which presented water as HO and hydrogen sulphide as HS, involved the anomaly that such formulæ represented two volumes of vapour, whilst HCl and NH_3 represented four volumes. The unitary system of formulæ was still unacceptable to the great majority of chemists, although many occupied themselves in testing the capacities of the several systems of types with a view to the discovery of relationships among the very numerous carbon compounds daily issuing from every laboratory. The water type of Williamson, the ammonia type of Wurtz and Hofmann, the hydrochloric acid and hydrogen types of Gerhardt afforded for some years a basis for discussion which, although ultimately fertile, inasmuch as it led indirectly to the idea of the linking of atoms, was too often barren enough for all immediate practical purposes. The time had not arrived when the property of atoms, which is now called valency, could be recognised, and although Frankland as early as 1852 (*Phil. Trans.*, 1852, **142**, 417) had drawn attention to the fact that the combining powers of elements are limited and constant, it remained until many years later among the numerous unutilised curiosities of observation. It might be said that those who made use of the water type and the ammonia type for various compounds implicitly admitted the idea that the oxygen and the nitrogen in these compounds respectively did hold together, in the one case two and in the other case three atoms. This, however, was not definitely recognised until much later, when, in 1858, Kekulé (*Annalen*, 1858, **106**, 129) and Couper (*Ann. Chim. Phys.*, 1858, **53**, 469; *Phil. Mag.*, 1858, [iv], **16**, 104) independently showed that in carbon compounds the element carbon must be the nucleus to which the other atoms are attached, and that atoms of carbon, in such compounds, must be united to one another.

At this point it would be, to say the least, unjust not to call to remembrance the great services to science rendered throughout this period by one who was then the junior secretary and is now the senior Fellow of the Chemical Society. If the expositions* addressed by Odling to the Society, and thence to the chemical world outside, failed to clear away much of the confusion and many of the anomalies then permeating theoretical chemistry, it was due to no lack of clearness of thought, knowledge of facts, or cogency of reasoning on the part of the lecturer, but rather to the conservative indisposition to change which often enchains the scientific world, in spite of the precepts of the science which it professes.

During all this long period the name of Avogadro had been treated with a neglect which is scarcely compensated by the recognition now accorded to it nearly a century after his time. Among the French, Ampère gets more credit in this connexion than seems to belong to him, for his paper (*Ann. Chim. Phys.*, 1814, **90**, 43) three years later than the memoir of Avogadro shows little evidence that he attached the same importance to the theorem that equal volumes of different gases under the same conditions contain the same number of particles as did Avogadro. The memoir of Ampère is chiefly devoted to a consideration of the probable forms of the "particules" (molecules) of crystallised substances.

Even those chemists who are generally supposed to have made use of Avogadro's idea have neglected all reference to its origin. Gerhardt, for example, ignored the Italian physicist, and Dumas in the paper on vapour densities already quoted only mentions his name in the following passage, which forms the conclusion of the memoir: "Nous sommes bien éloignés encore de l'époque où la

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* Especially "On the Atomic Weights of Oxygen and Water" (*Quart. Journ. Chem. Soc.*, 1858, **11**, 107).

chimie moléculaire pourra se diriger par des règles certaines, malgré les avantages immenses que cette partie de la philosophie naturelle a retirés des travaux de MM. Gay-Lussac, Berzelius, Dulong et Petit, Mitscherlich, ainsi des vues théoriques de MM. Ampère et Avogadro. L'activité singulière de M. Berzelius et le bon esprit des chimistes dont il a enrichi l'Allemagne pourraient cependant faire espérer sur ce sujet important une révolution prochaine et durable."

It was not, however, until thirty years later that this revolution was brought about, and its author was a chemist from no northern school. The year 1858 must for ever be distinguished in the history of chemistry, for it was then that Cannizzaro led the way out of the darkness in which all had been so long struggling.

After this preamble we may more easily realise the nature and extent of the revelation, as it may well be called, which students of chemistry owe to Cannizzaro. That it remained for some years almost unknown may be attributed in part to the barrier constituted by the language in which his essay was originally published. But it is not creditable to the chemists of 1860 that the Congress held at Carlsruhe in September of that year, at which Cannizzaro was present and expounded his views, should have dispersed without a general acceptance of the fundamental principles which to us seem unassailable. The only excuse which presents itself now is the fact that at this period the difficulties arising out of dissociation of compounds like sal-ammoniac and sulphuric acid when volatilised by heat, and which gave rise to the so-called anomalous vapour densities, had not been cleared away. To contend, as some speakers seem to have done, that these subjects are matters of opinion, and that every scientific man is entitled to perfect freedom in respect to the views he adopts, is to misunderstand the case. In art, in which field sentiment, emotion, and taste are the only considerations involved, complete freedom is clearly necessary, but in science whenever facts have been established and an agreement has been arrived at in regard to fundamental assumptions, reason ought to be the only, as it is the sufficient, guide. Unfortunately, this has not always been the case.

It is only fair to mention that of those chemists who were present at the Carlsruhe Congress in 1860, one at least came away convinced. In a prefatory note to the German edition (published in 1891) of Cannizzaro's "Sketch," Professor Lothar Meyer relates how he received at the meeting a copy of this paper, which he read with surprise at the clearness with which all the most important difficulties were removed. He says: "It was as though scales fell from my eyes, doubt vanished, and was replaced by a feeling of peaceful certainty." In 1864 Meyer published his well-known treatise on the "Modern Theories of Chemistry," in which the views of Cannizzaro are fully developed.

To those who have read Cannizzaro's "Sketch of a Course of Chemical Philosophy," of which a belated English translation has been produced by the Alembic Club, it must be a matter of wonder that the facts and arguments set forth should not have been sufficient to have cleared away the previous confusion immediately. With small and unimportant corrections, it represents a course of instruction which might have been given as embodying the accepted views of the chemical world down to quite recent times, and a perusal of this essay, even now, would be of the utmost value to many teachers.

Cannizzaro's "Sketch" begins with the following words*: "I believe that the progress of science made in these last years has confirmed the hypothesis of Avogadro, of Ampère, and of Dumas on the similar constitution of substances in the gaseous state; that is, that equal volumes of these substances, whether simple or compound, contain an equal number of molecules; not, however, an equal number of atoms, since the molecules of the different substances, or those of the same substance in its different states, may contain a different number of atoms, whether of the same or of diverse nature."

The author then proceeds to trace the history of this conception, of the consequences to chemical theory, and of the ideas which prevented the immediate acceptance of this hypothesis, and the confusion which resulted from the failure to distinguish molecules from atoms. In order to bring harmony into the various branches of chemistry, he then shows that by applying the hypothesis of Avogadro the weights of molecules may be determined before their composition is known, and that a knowledge of their composition is not necessary to this end. Having settled the molecular weights of a series of substances containing one element in common, the discovery is made that the different quantities of the same element contained in different molecules are always whole multiples of one and the same quantity, which represents the atomic weight. After studying the constitution of various volatile chlorides, bromides, and iodides, the question of the constitution of mercuric and mercurous compounds arises, and the author proceeds to show that the smallest proportion of mercury present in any molecule containing that element is 200, and that this is therefore the atomic weight of the metal. This number is then confirmed by appeal to the law of specific heats. The analogy of the chlorides

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* I have made use of the *Alembic Club* version in these quotations.

of copper with those of mercury next leads to the examination of these compounds, but as the vapour densities of these salts are not known, the specific heat of copper and of its compounds leads to the number 63 as the atomic weight of copper. Whether this is the molecular weight of the uncombined metal there is no means of knowing until the vapour density of this substance can be determined. Many other metals are then examined, and the author points out that in such cases as tin, which produces compounds volatile without decomposition, and of which the molecular weight can be determined, the atomic weight deduced from specific heat is in agreement with that deduced from vapour density. But then the question arises: "Are the atoms of all these metals equal to their molecules, or to a simple submultiple of them?" And he proceeds. "I gave you above the reasons which make me think it probable that the molecules of these metals are similar to that of mercury; but I warn you now that I do not believe my reasons to be of such value as to lead to that certainty which their vapour densities would give if we only knew them." Herein he differs from Gerhardt, who had represented the atoms of all the metals as fractions of the respective molecules, as in the case of hydrogen.

A little later Cannizzaro comes very near to the modern idea of valency when discussing the capacity of saturation of different atoms. When referring to diatomic radicals as "those which, not being divisible, are equivalent to two of hydrogen or to two of chlorine," he proceeds to show "that cacodyle, C_2H_6As, methyl, CH_3, ethyl, C_2H_5, and the other homologous and isologous radicals are like the atom of hydrogen, monatomic, and, like it, cannot form a molecule alone, but must associate themselves with another monatomic radical, simple or compound, whether of the same or of a different kind, and that ethylene, C_2H_4, propylene, C_3H_6, are diatomic radicals analogous to the radicals of mercuric and cupric salts, and to those of the salts of zinc, lead, calcium, magnesium, etc.; and that these radicals, like the atom of mercury, can form a molecule by themselves. The analogy between the mercuric salts and those of ethylene and propylene has not been noted, so far as I know, by any other chemist."

There is much more in the "Sketch" which was important for the elucidation of the views put forward by the author, but the extracts given are sufficient to show how clear, how systematic, and how logical was the mind which could thus choose out from the tangled mass of fact and fiction constituting chemical theory in his day, the materials for a consistent, orderly, and productive system of scientific chemistry.

What Cannizzaro did for chemistry may be broadly stated under the two following heads:

First, he laid down for all time the two principal methods by which atomic weights are determined, the one by reference to the molecular weights derived from an application of Avogadro's rule, and the other by the adoption of the principle originally discovered by Dulong and Petit as to the general relation of atomic weight to specific heat among the solid elements, and he showed that these two methods when applicable to the same case lead to the same results.

Secondly, he placed inorganic chemistry in a new light by applying to inorganic compounds the same principles which had been applied to organic compounds, and thus finally disposed of the superstition which had hovered so long in the minds of chemists that organic chemistry was subject to laws different from those prevailing among mineral substances.

There is, in fact, but one science of chemistry and one set of atomic weights.

It will not be without interest to recall some of the consequences of the ultimate adoption, tardy as it was, of the principles laid down by Cannizzaro. The unanimity which has prevailed among chemists during the last forty years or more as to the fundamental principles inculcated by Cannizzaro is a proof that his system is not only reasonable but is practically convenient. We are not now divided into parties on the subject of atomic weights, and although some may still incline to use hydrogen as the unit, whilst others prefer an exact integer for oxygen, these differences do not affect the notation nor the common language of chemistry. As a result of a uniform standard for atomic weights we now possess a natural system of classification of the known elements in the form of the periodic scheme with all its consequences, which I need not describe to a Society of chemists. Out of the revised and uniform system of atomic weights we also have a universally acknowledged system of constitutional formulæ, based on valency, which we may define as the habit in regard to combination exhibited by the several elementary atoms, without necessarily forming any hypothesis as to the cause or nature of chemical "affinity." The wonderful discoveries which have been brought to light in the department of stereochemistry provide a body of evidence in favour of atomic structure which can never be set aside; and the day is now gone by when serious support can be found for any form of anti-atomic doctrine, since we have been shown how single atoms can be seen and counted.

That all this knowledge would have come into the possession of mankind sooner or later cannot be doubted, but that this generation enjoys all the fruits of experiment in chemistry we owe to Cannizzaro. Without the clear light which his doctrine cast into the dark places of chemical theory sixty years ago chemistry might have remained a mass of unclassified, incoherent, and perplexing facts.

This is why it is incumbent on this generation of chemists to do honour to his memory. The Chemical Society cannot be charged with indifference to the great services rendered to science by Cannizzaro, for, as mentioned at the outset, his name was placed on the limited roll of Honorary Members of the Society so far back as 1862. Ten years later he was invited to give the second Faraday Lecture, and again in 1896, on the occasion of his seventieth birthday, an address was presented to him on behalf of the Society, in which full expression was given to the feelings of respect and admiration entertained by all the Fellows toward the veteran chemist.

The Royal Society, also, awarded to him in 1891 the Copley Medal, which is regarded as the highest honour in the power of the Society to bestow.

Although English chemists have thus given what may be called official recognition to the author of the great reform, it would be unbecoming in any of us to hint at indifference or injustice on the part of French or German chemical writers while there are large and prominent English treatises in which the name of Cannizzaro is not even mentioned. Surely this is an occasion when in remembrance of the unity of scientific thought throughout the world, fed by the contributions of all nations, a plea may be entered, not only for justice to individuals, but for complete international impartiality in matters of science.

Italian science is no mushroom growth. Before our own Royal Society was founded, or perhaps even thought of, before the French Academy of Sciences came into existence, Galileo and Torricelli were making discoveries of world-shaking significance. In those times, however, to have observed natural phenomena, and even to be suspected of holding unfamiliar, novel, and therefore heretical opinions about the world in which man is placed, was to draw down on the unhappy philosopher the condemnation of political and ecclesiastical ignorance and fanaticism. No wonder that those whose interest was excited by the new knowledge then coming to light endeavoured to conceal their discussions and places of meeting under all kinds of fantastic and often ridiculous masquerade.*

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* See, for example, Disraeli's *Curiosities of Literature*: "On the Ridiculous Titles assumed by the Italian Academies."

Happily such prejudice, although occasionally showing itself, as in the instance already mentioned of the publication of *Il Nuovo Cimento,* is now powerless, and the neglect of Avogadro's hypothesis cannot be put down to the influence of ecclesiastical authority. The obscurity which prevented its recognition arose out of the very nature of chemistry itself, and even the prosecution of research seemed for a time only to add to the prevailing confusion by producing crowds of new and unclassified facts. Science had, in fact, to wander in the wilderness until the great leader came to show the way. That Avogadro's life should have come to a close only two years before the formal proclamation and application of his doctrine before a congress of chemists seems a harsh dispensation, but if he had lived only a little longer it would surely have been to him an added satisfaction that that doctrine should have been established by his fellow-countryman.

As to Cannizzaro himself, we may rejoice that he not only led chemistry out of the shadow of the pillar of cloud, but in living to see the complete triumph of the system he had laid down so long ago he truly entered into the enjoyment of the promised land.

On the scutcheon which bears the names of Galileo and Torricelli, of Galvani and Volta, of Avogadro and Piria, Italy may proudly write another glorious name, STANISLAO CANNIZZARO.

CLXXVIII.—*The Action of Sulphur on Amines. Part I. o-Toluidine.*

By HERBERT HENRY HODGSON, M.A., B.Sc., Ph.D.

THE action of sulphur on amines is one which has occupied the chemists of a past generation very extensively. Latterly, however, investigation appears to have been focussed on the interaction of complex mixtures for the purpose of obtaining valuable dyestuffs. The present paper is the first of a series of contributions the object of which is to reopen the whole subject.

The subject of this paper, *o*-toluidine, has been chosen first because the results obtained are of such an important character as to afford an insight into the more complex problem of the action of sulphur on aniline. A subsequent paper, the details of which are at present under investigation, will deal with aniline and its reaction products under varying conditions.

Merz and Weith (*Ber.*, 1871, **4**, 384), in their pioneering work, discovered thioaniline by the interaction of aniline with sulphur and lead oxide; also thiotoluidine by heating *p*-toluidine under the same conditions. Gattermann found (*Ber.*, 1889, **22**, 424; 1892, **25**, 1084) that by heating sulphur with *p*- or *o*-toluidine for eighteen hours at 180—190° he obtained dehydrothio-*p*-toluidine and dehydrothio-*o*-toluidine respectively. Bayer & Co. (English Patent 6319 of 1888) prepared a dithio-*p*-toluidine by heating excess of sulphur with *p*-toluidine at elevated temperatures (250°). K. A. Hofmann (*Ber.*, 1894, **27**, 2807) found that by heating aniline for twelve hours with sulphur at 170—180° he obtained di-*o*-thioaniline, whilst when hydrochloric acid was present the reaction took place with much greater rapidity and with the formation of di-*p*-thioaniline. Hinsberg (*Ber.*, 1905, **38**, 1130), repeating Hofmann's work and introducing suitable improvements, found the reaction to be of a very complex character, at least four crystalline substances being produced, namely, diphenylamine, dithioaniline, Merz's thioaniline, and a new thioaniline.

In the case of *o*-toluidine the present author found, by heating it at 180—190° with sulphur for three to four hours, that practically no action had taken place. This reaction is at present under investigation.

It appears from previous work that the action of sulphur alone on aniline and the toluidines is not very vigorous, only taking place slowly at elevated temperatures and after prolonged heating. When, however, some other substances are present, such as lead oxide, hydrochloric acid, etc., interaction readily takes place. The present paper deals with the action of sulphur on *o*-toluidine in the presence of hydrochloric acid, whereby a single product appears to be formed. The reaction takes place best when 100 grams of *o*-toluidine, 50 grams of *o*-toluidine hydrochloride (or the equivalent amounts of concentrated hydrochloric acid and *o*-toluidine), and 50 grams of sulphur are heated for two to three hours at 180—190°. More prolonged heating or elevated temperature only deteriorates the yield and quality of the reaction product. Analyses indicate that the substance formed, which is readily isolated by means of its hydrochloride, is a *trithio*-o-*toluidine*. This compound is capable of reduction by the ordinary reducing agents forming a *dithio*-o-*toluidine*.

Although the hydrochloride is a crystalline compound, the other derivatives studied appear to be amorphous, since efforts to crystallise them have proved unsuccessful. They all appear to possess lower melting points than the corresponding dithio-compounds.

The importance of the reaction lies in the fact that a trithio-compound is formed, and present results appear to indicate that such is the case in the analogous aniline reaction. If the latter proves to be the case, then valuable data are to hand for the explanation of the various differences observed between the results of previous investigators when only small divergences are made in the reaction conditions.

Nitric acid appears to direct the reaction in the same way as hydrochloric.

In view of the quantitative character of the yield with *o*-toluidine, and the apparent complexity of the reaction with several other amines, it appears probable that the ortho-position may exert a directing influence on the mode of substitution. This point is at present receiving careful attention.

The dyestuffs obtained by diazotisation and coupling with such components as α-naphthol-4-sulphonic acid deserve special mention on account of their extraordinary fastness. Whilst having little or no affinity for the cotton fibre on the one hand, they are easily taken up by wool, giving shades of remarkable fastness to milling, potting,* bleaching, stoving, acids, alkalis, and light. Moreover, this property of conferring fastness appears to be a fundamental characteristic of the whole series of bases.

EXPERIMENTAL.

Trithio-o-*toluidine Hydrochloride*, $S_3(CH_3\cdot C_6H_3\cdot NH_2)_2,2HCl$.

For the preparation of this compound, 100 grams of *o*-toluidine, 50 grams of *o*-toluidine hydrochloride, and 50 grams of sulphur are heated together at 185—190° for two to three hours. Should the higher temperature be much exceeded, then the resulting product is liable to be of a tarry character. Further extension of the heating period is unnecessary in view of the almost quantitative character of the yield. The fusion is then rendered faintly alkaline by means of sodium hydroxide, and subjected to steam distillation until no further unattached *o*-toluidine passes over. The contents are then diluted to about 500 c.c., and, after being neutralised, are heated on the water-bath with about 100 c.c. of concentrated hydrochloric acid (D 1·15). The hot acid liquor, which contains the bulk of the reaction product in solution, is filtered and allowed to cool. The hydrochloride of a base rapidly separates with falling temperature in almost quantitative yield. The substance, which is crystalline in character, was recrystallised several times from hot dilute hydrochloric acid, and then melted at 226—227° (uncorr.).

The above crystalline separation is practically a pure compound when first obtained, and on analysis appears to be the hydrochloride of a trithio-*o*-toluidine.

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* The term "potting," which has a varied industrial significance, is here restricted to the action of hot and cold water on the dyed fabric.

This hydrochloride is almost insoluble in cold water, more readily soluble in hot, but somewhat easily if the water is slightly acidulated with hydrochloric acid. There appears to be a definite acid concentration for ready solubility, above or below which the compound is very sparingly soluble. In moderately concentrated hydrochloric acid the compound is practically insoluble. The hydrochloride is also insoluble in ether and the usual solvents, whilst in hot alcohol it is sparingly soluble.

On diazotisation, the hydrochloride readily forms a soluble, yellow bisdiazo-compound, which is capable of uniting with the usual azo-dyestuff components to form dyestuffs possessing an exceedingly fast character.

In warm hydrochloric acid solution hydrogen sulphide exerts a slow reducing effect with precipitation of sulphur. Concentrated nitric acid acts vigorously on the substance, forming a brownish-red solution. On warming the hydrochloride with concentrated sulphuric acid, the solution becomes pale green, turning to olive-green, and on pouring into water a reddish-violet colour appears. When heated with dilute hydrochloric acid and potassium dichromate, a brownish-black precipitate is formed. In cold aqueous hydrochloric acid solution, lead peroxide produces a slight violet colour, which rapidly turns brownish-black. In alcoholic hydrochloric acid solution the above colour changes are much more prominent. In hot alcoholic hydrochloric acid solution lead peroxide rapidly produces a reddish-violet colour, which changes to deep red.

The substance when obtained crystalline from hydrochloric acid solution possesses a very light brown colour, which deepens with age:

0·1916 gave 12 c.c. N_2 (moist) at 20° and 740 mm. $N=6·97$.
0·1762 „ 0·3219 $BaSO_4$. $S=25·08$.
0·12 „ 0·883 AgCl. $HCl=18·71$.
$C_{14}H_{16}N_2S_3,2HCl$ requires $N=7·34$; $S=25·19$; $HCl=19·16$ per cent.

Trithio-o-toluidine, $S_3(CH_3·C_6H_3·NH_2)_2$.

The free base is liberated as a resinous mass from the hydrochloride by means of alkali. All attempts to crystallise it have up to the present been unsuccessful. The corresponding aniline analogue, trithioaniline, is also a resinous substance according to Beilstein.

The resinous base was dissolved in benzene, and to this solution light petroleum was added from time to time, when a resinous mass separated, which on keeping became a yellow, amorphous solid; this melted at 90°, after sintering at about 74°.

The solid base is almost insoluble in water or light petroleum, moderately soluble in ethyl acetate, and readily so in alcohol, ether, acetone, benzene, chloroform, or carbon tetrachloride.

On warming with concentrated sulphuric acid, the solution becomes pale green, turning to olive-green, and on dilution this changes to red. Alcoholic lead peroxide gives a greenish-brown colour, turning to reddish-brown:

0·22 gave 0·4744 $BaSO_4$. S=29·7.

$C_{14}H_{16}N_2S_3$ requires S=31·16 per cent.

Trithio-o-*toluidine Sulphate*, $S_3(CH_3{\cdot}C_6H_3{\cdot}NH_2)_2,H_2SO_4$.

This was prepared by adding an alcoholic solution of concentrated sulphuric acid to a solution of trithio-*o*-toluidine in chloroform. The amorphous precipitate was collected and dried. It is almost insoluble in hot or cold water, very sparingly soluble in alcohol, but readily so in hot dilute hydrochloric acid:

0·1870 gave 0·4303 $BaSO_4$. S=32·13.

$C_{14}H_{16}N_2S_3,H_2SO_4$ requires S=31·53 per cent.

Trithio-o-*toluidine Oxalate*, $S_3(CH_3{\cdot}C_6H_3{\cdot}NH_2)_2,C_2H_2O_4$.

This compound may be prepared either by dissolving the free base in hot oxalic acid, and allowing the solution to cool, or by dissolving the hydrochloride in hot water faintly acidulated with hydrochloric acid, and after adding excess of oxalic acid, allowing the solution to cool. A white, amorphous precipitate separates, which is sufficiently pure for analysis. The compound is insoluble in cold water, moderately soluble in hot water or hot alcohol, very sparingly so in ether, and insoluble in benzene. It melts at 156—157° (uncorr.):

0·1331 gave 0·2352 $BaSO_4$. S=24·26.

$C_{14}H_{16}N_2S_3,C_2H_2O_4$ requires S=24·12 per cent.

Action of Acetic Anhydride on the Base.

The action of acetic anhydride on the base appears to be more than a replacement of a hydrogen atom in the amino-groups, according to the conditions employed. If the base is boiled with acetic anhydride for a moderate period, then the action appears to be disruptive, since analyses indicate the formation of the acetyl derivative of dithio-*o*-toluidine.

If, however, the base is heated gently for a few minutes on the water-bath with acetic anhydride, then the acetyl derivative of the trithio-compound, $S_3(CH_3{\cdot}C_6H_3{\cdot}NHAc)_2$, appears to be formed. It was isolated by pouring the cooled reaction product into water, and allowing it to remain until solid. The solid was then dissolved in glacial acetic acid, and again precipitated by water. Attempts to crystallise it have hitherto failed. The substance possesses a slight purplish tint, due to the presence of traces of colouring matters, and melts at 120—130°.

The compound is almost insoluble in boiling water, insoluble in ether, light petroleum, or benzene, readily soluble in glacial acetic acid or alcohol, and sparingly so in dilute acetic acid:

0·1926 gave 0·3457 $BaSO_4$. S=24·64.

$C_{18}H_{20}O_2N_2S_3$ requires S=24·49 per cent.

The action of acetic anhydride is still under investigation.

*Benzoyl Derivative of Trithio-*o*-toluidine*, $S_3(CH_3{\cdot}C_6H_3{\cdot}NHBz)_2$.

This derivative was prepared by adding a benzene solution of benzoyl chloride to one of the base, together with a few drops of dimethylaniline. The product was washed successively with dilute sodium hydroxide, hydrochloric acid, water, alcohol, and light petroleum. The solid was then recrystallised either from benzene or alcohol, when it melted at 187° (uncorr.).

The substance is sparingly soluble in cold benzene, more readily in hot, whilst it is fairly readily soluble in hot alcohol, and insoluble in light petroleum:

0·2113 gave 0·2870 $BaSO_4$. S=18·62.

$C_{28}H_{24}O_2N_2S_3$ requires S=18·60 per cent.

m-*Nitrobenzylidinetrithio*-o-*toluidine*,
$S_3(CH_3{\cdot}C_6H_3{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2)_2$.

One gram of *m*-nitrobenzaldehyde (2 mols.) and 1 gram of the base were dissolved in hot alcohol, the solutions mixed together, and heated for several minutes on the water-bath. After a short interval a yellow solid separated, which was dissolved in benzene and reprecipitated as a greenish-yellow powder by the careful addition of light petroleum. Attempts at crystallisation proved unsuccessful. The substance melts at 136° (uncorr.), after sintering at 132°. In water, alcohol, ether, and light petroleum the substance is insoluble; it is moderately soluble in carbon tetrachloride or cold acetone, and readily so in hot acetone, benzene, toluene, chloroform, or warm glacial acetic acid. It dissolves in concentrated sulphuric acid to a brilliant yellow solution, which on heating darkens to olive-green:

0·1417 gave 0·1749 $BaSO_4$. S=16·95.

$C_{28}H_{22}O_4N_4S_3$ requires S=16·72 per cent.

Trithio-o-toluenebisazo-β-naphthol, $S_3(CH_3 \cdot C_6H_3 \cdot N_2 \cdot C_{10}H_7 \cdot OH)_2$.

This brilliant red compound was prepared by diazotising the hydrochloride in the usual way, and coupling in alkaline solution with β-naphthol. The red precipitate so formed was well washed with water, alcohol, and ether, and dissolved in boiling carbon tetrachloride solution, in which it is fairly soluble. On cooling an amorphous substance separated, which could not be crystallised. The red compound melts at 118°, probably with decomposition. It is insoluble in water or light petroleum, very sparingly soluble in alcohol, acetone, or ether, moderately so in hot benzene, carbon tetrachloride, or glacial acetic acid, and readily so in hot chloroform. Concentrated sulphuric acid in the cold produces a beautiful violet colour, which becomes scarlet on dilution with water. On heating, the violet colour changes to chocolate, which on dilution becomes brownish-red:

0·2094 gave 0·2476 $BaSO_4$. S=16·23.

$C_{34}H_{28}O_2N_4S_3$ requires S=15·53 per cent.

Reduction of Trithio-o-toluidine Hydrochloride.

The hydrochloride was dissolved in hot dilute hydrochloric acid, and to the deep brownish-yellow solution so obtained zinc dust was added, when a violet action ensued, hydrogen sulphide being copiously evolved. After the reaction had subsided, the contents were gently heated on the water-bath until the solution became colourless, zinc dust being added from time to time. A 10 per cent. solution of sodium hydroxide was then added until alkalinity was attained, whereby the bulk of the reaction products remained in solution. After filtration the solution was allowed to remain for some time, when a crystalline substance separated. The formation of the latter could be accelerated by bubbling air through the solution or by the addition of mild oxidising agents. The substance after recrystallisation from dilute alcohol proved to be a dithio-*o*-toluidine.

Dithio-o-toluidine, $S_2(CH_3 \cdot C_6H_3 \cdot NH_2)_2$.

The base crystallises from dilute alcohol in colourless clusters melting at 112°. It is insoluble in water or light petroleum, readily soluble in alcohol, ether, ethyl acetate, acetone, benzene, toluene, chloroform, carbon tetrachloride, or glacial acetic acid. Cold concentrated sulphuric acid first produces a violet colour, which increases in intensity on warming, changing to blue, and then green. On dilution the solution becomes red. In alcoholic solution lead peroxide produces a dark brown colour on warming. In alcoholic solution acidulated with hydrochloric acid, lead peroxide produces a chocolate colour in the cold, which on heating becomes darker, changing to deep brownish-red on keeping. Hydrogen sulphide decolorises the greenish-yellow solution, the base being reduced to mercaptan, as proved by the solubility in sodium hydroxide. The reduction product is easily changed into the original base by mild oxidising agents:

0·2139 gave 0·3655 $BaSO_4$. S=23·46.

$C_{14}H_{16}N_2S_2$ requires S=23·18 per cent.

Dithio-o-*toluidine Hydrochloride*, $S_2(CH_3\cdot C_6H_3\cdot NH_2)_2,2HCl$.

This compound is obtained in beautiful, colourless needles or clusters by adding concentrated hydrochloric acid to an alcoholic solution of the base, and allowing to remain for a short interval, or by adding concentrated hydrochloric acid to a solution of the base in dilute acid. It is sparingly soluble in cold water, but fairly so in hot, from which it crystallises in fine, hair-like needles, melting at 256—257° (uncorr.). In cold alcohol it is insoluble, as also in ether or benzene, whilst it is moderately soluble in boiling alcohol:

0·1248 gave 0·1628 $BaSO_4$. S=17·91.

$C_{14}H_{16}N_2S_2,2HCl$ requires S=18·33 per cent.

Dithio-o-*toluidine Sulphate*, $S_2(CH_3\cdot C_6H_3\cdot NH_2)_2,H_2SO_4$.

This is prepared by adding an alcoholic solution of sulphuric acid to a concentrated alcoholic solution of the base. It is a white, crystalline solid of very insoluble character:

0·1459 gave 0·2684 $BaSO_4$. S=25·26.

$C_{14}H_{16}N_2S_2,H_2SO_4$ requires S=25·66 per cent.

Dithio-o-*toluidine Oxalate*, $S_2(CH_3\cdot C_6H_3\cdot NH_2)_2,C_2H_2O_4$.

This compound is prepared by dissolving the base in hot oxalic acid, and allowing the filtered solution to cool slowly. The solid which separates is crystallised from hot water containing oxalic acid, when it melts at 165°. It is more insoluble in hot water than the corresponding trithio-compound, and is insoluble in alcohol:

0·1265 gave 0·1578 $BaSO_4$. S=17·12.

$C_{14}H_{16}N_2S_2,C_2H_2O_4$ requires S=17·48 per cent.

Acetyl Derivative of Dithio-o-*toluidine*, $S_2(CH_3\cdot C_6H_3\cdot NHAc)_2$.

On adding acetic anhydride to the finely powdered base in sufficient quantity to form a concentrated solution, and then gently warming on the water-bath, the contents passed into solution. On cooling, the reaction product separated, and was crystallised from hot glacial acetic acid, when it melted at 224—225° (uncorr.). In water, benzene, or ether it is practically insoluble, in alcohol or cold glacial acetic acid moderately soluble, and it is readily so in hot glacial acetic acid:

0·1436 gave 0·1848 $BaSO_4$. S=17·67.

$C_{18}H_{20}O_2N_2S_2$ requires S=17·77 per cent.

m-*Nitrobenzylidinedithio*-o-*toluidine*, $S_2(CH_3\cdot C_6H_3\cdot N{:}CH\cdot C_6H_4\cdot NO_2)_2$.

m-Nitrobenzaldehyde (2 mols.) and dithio-*o*-toluidine (1 mol.) were dissolved in hot alcohol, the solutions mixed together, and heated for several minutes on the water-bath, when a yellow solid began to separate. After some time this was crystallised from toluene, from which it separated in greenish-yellow, crystalline clusters, melting at 173° (uncorr.). In water, alcohol, ether, or light petroleum the substance is insoluble; in acetone, hot glacial acetic acid, or carbon tetrachloride it is sparingly soluble (compare the corresponding trithio-derivative), but is fairly readily dissolved by benzene, toluene, or chloroform. It dissolves in concentrated sulphuric acid to a brilliant yellow solution, which on warming darkens to olive-green:

0·1719 gave 0·1445 $BaSO_4$. S=11·54.

$C_{28}H_{22}O_4N_4S_2$ requires S=11·80 per cent.

Dithio-o-*toluenebisazo-β-naphthol*, $S_2(CH_3\cdot C_6H_3\cdot N_2\cdot C_{10}H_7\cdot OH)_2$.

This brilliant red compound was prepared exactly like the corresponding trithio-derivative. The purified, amorphous substance melts at 248°. It is insoluble in water, ether, or light petroleum, sparingly soluble in alcohol or acetone, moderately so in hot carbon tetrachloride or glacial acetic acid, and readily so in hot benzene, toluene, or chloroform. With concentrated sulphuric acid in the cold it turns bluish-violet, changing to scarlet on dilution. On warming with concentrated sulphuric acid the colour changes to violet-red, becoming brownish-red on dilution:

0·1269 gave 0·1056 $BaSO_4$. S=11·42.

$C_{34}H_{28}O_2N_4S_2$ requires S=10·92 per cent.

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CLXXIX.—*The Resolution of* sec.-*Butylamine into Optically Active Components.*

By William Jackson Pope and Charles Stanley Gibson.

For some reason which is at present unknown, compounds of very simple constitution which presumably possess enantiomorphous molecular configurations are frequently not resolvable into optically active components by the ordinary methods; thus, Pope and Read were unable to resolve chlorosulphoacetic acid, $SO_3H{\cdot}CHCl{\cdot}CO_2H$, and chlorobromomethanesulphonic acid, $CHClBr{\cdot}SO_3H$ (Trans., 1908, **93**, 794), which contain asymmetric carbon atoms in the molecule, and also methylethylpropyl*iso*butylammonium iodide (this vol., p. 519), one of the simplest compounds which contains an asymmetric quinquevalent nitrogen atom. Gadamer and Urban (*Arch. Pharm.*, 1904, **242**, 48, 51), who prepared and examined a large number of derivatives of *sec.-d*-butylamine of natural origin, observed that they were unable to resolve the externally compensated base by crystallisation with optically active lactic, quinic, mandelic, and bromocamphorsulphonic acids, whilst Thomé (*Ber.*, 1903, **36**, 582) resolved the amine by the aid of *d*-tartaric acid. The failure of Gadamer and Urban to resolve the amine by crystallisation with a number of optically active acids suggested that *sec.*-butylamine resists resolution in much the same way as do the substances examined by Pope and Read, and we therefore subjected the synthetic base to a fresh examination with a view to obtain a clue to the abnormal behaviour mentioned. It was found, however, that the base is readily resolved by crystallisation with *d*-α-bromocamphor-π-sulphonic acid, and we are consequently able to describe the following method for the preparation of the optically active *sec.*-butylamines.

Externally Compensated sec.-*Butylamine*, $C_2H_5(CH_3)CH{\cdot}NH_2$.

Commercial methyl ethyl ketone is repeatedly distilled through column until the boiling point is constant, and the purity of th product checked by the preparation of the semicarbazide (Scholtz *Ber.*, 1896, **29**, 610); the purified ketone is then converted int methyl ethyl ketoxime as described by Janny (*Ber.*, 1882, **15** 2779).

The oxime (105 grams), dissolved in alcohol (900 c.c.), is heate to 40° in a water-bath, and sodium amalgam (5250 grams of 2·7 pe cent.), together with glacial acetic acid (505 grams), graduall added; the mixture is mechanically stirred, and the addition sodium amalgam and acetic acid so adjusted that the solution remains feebly acid. The reduction is complete in two days, and after distilling off the alcohol the residue is rendered alkaline and distilled in a current of steam, the distillate being collected in dilute hydrochloric acid; after evaporating the product to dryness the residue is distilled with addition of concentrated sodium hydroxide, and the resulting base fractionally distilled from solid potassium hydroxide. *sec.*-Butylamine is thus obtained, boiling at 66—68°/772 mm.

The *platinichloride*, $(CHMeEt{\cdot}NH_2)_2,H_2PtCl_6$, is fairly soluble in water, and crystallises from alcohol or ethyl acetate in orange-yellow, glistening plates, melting and decomposing at 228°:

0·3100 gave 0·1088 Pt. Pt=35·10.

$(C_4H_{11}N)_2,H_2PtCl_6$ requires Pt=35·09 per cent.

dl-*Benzoyl*-sec.-*butylamine*, $CHMeEt{\cdot}NH{\cdot}CO{\cdot}C_6H_5$.

This substance is readily obtained by the Schotten-Baumann reaction, and crystallises from aqueous alcohol in long, colourless needles, melting at 75—76°; it is very soluble in alcohol, benzene, ether, or ethyl acetate:

0·1112 gave 0·3032 CO_2 and 0·0870 H_2O. C=74·35; H=8·75.

$C_{11}H_{15}ON$ requires C=74·54; H=8·54 per cent.

dl-*Benzenesulphonyl*-sec.-*butylamine*, $CHMeEt{\cdot}NH{\cdot}SO_2{\cdot}C_6H_5$.

Benzenesulphonyl chloride reacts readily with *sec.*-butylamine in presence of aqueous potassium hydroxide, and the product, after crystallisation from a mixture of light petroleum and ether, forms long, colourless needles, which melt at 68°, and closely resemble the crystals of the corresponding benzoyl derivative. The compound is extremely soluble in the ordinary organic solvents with the exception of light petroleum:

0·1106 gave 0·2292 CO_2 and 0·0736 H_2O. C=56·49; H=7·45.

$C_{10}H_{15}O_2NS$ requires C=56·28; H=7·09 per cent.

dl-p-*Toluenesulphonyl*-sec.-*butylamine*, $CHMeEt{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4{\cdot}CH_3$.

This substance is obtained in quantitative yield by the Schotten-Baumann reaction, and separates from a mixture of light petroleum and ether in beautiful, colourless prisms, melting at 54—55°; it is readily soluble in the ordinary organic solvents, with the exception of light petroleum:

0·1641 gave 0·3462 CO_2 and 0·1128 H_2O. C=57·60; H=7·60.

$C_{11}H_{17}O_2NS$ requires C=58·10; H=7·54 per cent.

Resolution of dl-sec.-*Butylamine.*

l-sec.-*Butylamine* d-α-*Bromocamphor*-π-*sulphonate*, $CHMeEt{\cdot}NH_2,C_{10}H_{14}BrO{\cdot}SO_3H,H_2O$.

Externally compensated *sec.*-butylamine is dissolved in twice its volume of water, and the solution neutralised by the addition of the requisite amount of *d*-α-bromocamphor-π-sulphonic acid; after evaporation to a syrup, with addition of a small quantity of the base to replace that lost as a result of hydrolytic dissociation, the solution is allowed to remain in a vacuum desiccator. Crystallisation soon sets in, and when the residue has become as solid as possible the whole product is recrystallised from anhydrous ethyl acetate; successive fractions deposited from this solvent, in one particular operation, gave the following specific rotatory powers in 1·5 per cent. aqueous solutions: $[\alpha]_{\text{Hg green}}+80{\cdot}34°$, $+81{\cdot}28°$, $+81{\cdot}43°$, $+82{\cdot}26°$, $+84{\cdot}64°$, and $+85{\cdot}51°$ respectively; a considerable quantity of salt remained in the residual mother liquor, and could not be readily separated by crystallisation.

The crystalline fractions just referred to were recrystallised until constant in rotatory power and melting point; the product thus obtained proved to be pure *l-sec.*-butylamine *d*-α-bromocamphor-π-sulphonate. The substance separates from ethyl acetate in colourless, glistening needles, melting at 104—106°; it is very soluble in alcohol or water, but less so in ethyl acetate or acetone:

0·1764 gave 0·2728 CO_2 and 0·1086 H_2O. C=41·60; H=6·89.
0·1266 „ 0·1942 CO_2 „ 0·0786 H_2O. C=41·83; H=6·95.
$C_{14}H_{26}O_4NBrS,H_2O$ requires C=41·77; H=7·02 per cent.

The following determinations of rotatory power were made with an aqueous solution of 0·4652 gram in 29·94 c.c. at 20° in a 4-dcm. tube:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α..................	+4·95	+4·19°	+3·97°
[α]	+79·6	+67·4	+63·9
[M]	+320·3	+271·1	+256·8

Rotatory dispersions: $Hg_{\text{green}}/Na_{\text{yellow}}=1{\cdot}247$; $Hg_{\text{yellow}}/Na_{\text{yellow}}=1{\cdot}055$.

The molecular rotatory powers of ammonium *d*-α-bromocamphor-π-sulphonate in dilute aqueous solution for the three wave-lengths named above are respectively [M] +346·5°, +295·2°, and +278·7° (Pope and Read, Trans., 1910, **97**, 2201); the differences between the latter values and those for the above-described salt would indicate that the *l-sec.*-butylammonium ion has a considerable molecular rotatory power in dilute aqueous solution. Determinations made with the hydrochloride of the base show, however, that the basic ion has but a small molecular rotatory power, so that the molecular rotatory power of the bromocamphorsulphonate is anomalous.

d-sec.-*Butylamine* l-α-*Bromocamphor*-π-*sulphonate.*

Since *d-sec.*-butylamine *d*-α-bromocamphor-π-sulphonate proved difficult to crystallise, it was found convenient to distil all the residues obtained during the isolation of the above-described salt in a current of steam with addition of barium hydroxide; the distillate is then evaporated to dryness after neutralisation with *l*-α-bromocamphor-π-sulphonic acid, and the crystalline residue left to harden in a vacuum desiccator. After crystallisation from ethyl acetate as described above, pure *d-sec.*-butylamine *l*-α-bromocamphor-π-sulphonate is obtained, and is found to exhibit ordinary physical properties identical with those of the enantiomorphously related substance:

0·1174 gave 0·1798 CO_2 and 0·0730 H_2O. C=41·77; H=6·92.

$C_{14}H_{26}O_4NBrS,H_2O$ requires C=41·77; H=7·02 per cent.

The following rotatory-power determinations were made in an aqueous solution containing 0·4574 gram in 29·94 c.c. at 20° in a 4-dcm. tube:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α.................	−4·87°	−4·12°	−3·90°
[α]	−79·7	−67·4	−63·8
[M]	−320·5	−271·1	−256·6

Rotatory dispersions: Hg_{green}/Hg_{yellow}=1·248; Hg_{yellow}/Na_{yellow}=1·056.

It will be observed that the rotatory-power determinations made with this salt, *dBlA*, agree very closely with those quoted previously for the enantiomorphously related salt, *lBdA*, so that it is obvious that the two salts have been obtained in a state of purity.

l-sec.-*Butylamine*, CHMeEt·NH_2.

On distilling *l-sec.*-butylamine *d*-α-bromocamphor-π-sulphonate with addition of barium hydroxide in a current of steam, an aqueous solution of the base is obtained; a solution thus prepared, which was found by titration to contain 1·407 grams of base in 29·94 c.c., gave the following determinations of rotatory power in a 4-dcm. tube at 20°:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α.................	−1·08°	−0·98°	−0·94°
[α]	−5·75	−5·22	−5·00
[M]	−4·20	−3.81	−3·66

Rotatory dispersions: Hg_{green}/Na_{yellow}=1·150; Hg_{yellow}/Na_{yellow}=1·043.

The observation of Thomé, Gadamer, and Urban to the effect that the rotatory power of the base is opposite in sign to that of the salts with optically inactive acids, is thus confirmed.

l-sec.-*Butylamine Hydrochloride*, $CHMeEt{\cdot}NH_2,HCl$.

This salt was obtained by evaporating a solution of the base to dryness with excess of hydrochloric acid, and crystallising the residue from acetone; it forms long, silky needles having the properties described by Thomé. The following determinations were made in aqueous solutions in 4-dcm. tubes at 20°, the weights named being made up to 30 c.c. with the solvent:

Weight in grams.		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
1·0202	α	+0·17°	+0·13°	+0·12°
	[α]	+1·25	+0·96	+0·88
	[M]	+1·37	+1·05	+0·97

$Hg_{green}/Na_{yellow} = 1{\cdot}417$; $Hg_{yellow}/Na_{yellow} = 1{\cdot}083$.

1·0770	α	+0·18°	+0·14°	+0·13°
	[α]	+1·26	+0·97	+0·90
	[M]	+1·37	+1·07	+0·99

$Hg_{green}/Na_{yellow} = 1{\cdot}385$; $Hg_{yellow}/Na_{yellow} = 1{\cdot}077$.

The second series of determinations quoted above was made with the material used in the first series after it had been subjected to several recrystallisations from acetone containing a little alcohol; the close agreement between the two sets of values indicates that they refer to the pure salt.

Benzoyl-d-sec.-*butylamine*, $CHMeEt{\cdot}NH{\cdot}CO{\cdot}C_6H_5$.

This substance is conveniently prepared by the Schotten-Baumann reaction from *d-sec.*-butylamine *l*-α-bromocamphor-π-sulphonate, and after several recrystallisations from aqueous alcohol is obtained in long, colourless needles, melting at 92°; its melting point is thus considerably higher than that of the externally compensated isomeride, namely, 75—76°. The compound is readily soluble in alcohol, ethyl acetate, and benzene:

0·1214 gave 0·3326 CO_2 and 0·0960 H_2O. C = 74·71; H = 8·85.

$C_{11}H_{15}ON$ requires C = 74·54; H = 8·64 per cent.

The following determinations of rotatory power were made in an alcoholic solution containing 0·3002 gram in 29·94 c.c. in a 4-dcm. tube at 20°:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α................	+1·49°	+1·29°	+1·23°
[α]	+37·1	+32·2	+30·7
[M]	+65·8	+57·0	+54·3

$Hg_{green}/Na_{yellow} = 1{\cdot}212$; $Hg_{yellow}/Na_{yellow} = 1{\cdot}049$.

Benzenesulphonyl-d-sec.-*butylamine*, $CHMeEt{\cdot}NH{\cdot}SO_2{\cdot}C_6H_5$.

This compound, also prepared by the Schotten-Baumann reaction, is purified by recrystallisation from light petroleum; it forms long, silky needles, melting at 62—63°, and is readily soluble in the ordinary organic solvents with the exception of light petroleum:

0·1136 gave 0·2345 CO_2 and 0·0725 H_2O. C=56·28; H=7·14.
$C_{10}H_{15}O_2NS$ requires C=56·28; H=7·09 per cent.

The rotation constants were determined in an alcoholic solution containing 0·9034 gram in 29·94 c.c. in a 4-dcm. tube at 20°:

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$
α	+0·30°	+0·30°	+0·29°
[α]	+2·49	+2·49	+2·40
[M]	+5·30	+5·30	+5·12

p-*Toluenesulphonyl*-d-sec.-*butylamine*, $CHMeEt{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4{\cdot}CH_3$.

This substance, prepared with the aid of *p*-toluenesulphonyl chloride, is purified by recrystallisation from light petroleum; it forms colourless prisms melting at 60—61°, and is very soluble in the ordinary organic solvents:

0·1219 gave 0·2610 CO_2 and 0·0851 H_2O. C=58·39; H=7·81.
$C_{11}H_{17}O_2NS$ requires C=58·10; H=7·54 per cent.

The following determinations of rotatory power were made in an alcoholic solution containing 0·9064 gram in 29·94 c.c. in a 4-dcm. tube at 20°:

	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
α	+0·10°	+0·10°	+0·10°
[α]	+0·81	+0·81	+0·81
[M]	+1·83	+1·83	+1·83

It is very noteworthy that this substance exhibits no rotatory dispersion in alcoholic solution, so that its rotation constants can be determined in white light; it is further to be remarked that the previously described benzenesulphonyl derivative also shows no appreciable dispersion, although benzoyl-*d*-sec.-butylamine possesses quite an ordinary rotatory dispersion. It seemed therefore desirable to examine some other acidic sulphonyl derivative of *d-sec.*-butylamine for the purpose of ascertaining whether this class of compounds are in general devoid of rotatory dispersion.

Naphthalene-α-sulphonyl-l-sec.-*butylamine*, $CHMeEt{\cdot}NH{\cdot}SO_2{\cdot}C_{10}H_7$.

Equivalent quantities of *l-sec.*-butylamine *d*-α-bromocamphor-π-sulphonate, naphthalene-α-sulphonyl chloride, and potassium hydroxide readily react in aqueous solution to yield a solid product; the latter, after recrystallisation from aqueous alcohol, is obtained in long, glistening needles, melting at 134—135°. The compound is not so readily soluble as the sulphonyl derivatives described above, but is fairly easily soluble in the ordinary organic solvents:

0·1055 gave 0·2470 CO_2 and 0·0590 H_2O. C=63·85; H=6·26.

$C_{14}H_{17}O_2NS$ requires C=63·82; H=6·51 per cent.

The rotatory power was determined in an alcoholic solution containing 0·8196 gram in 30·0 c.c. in a 4-dcm. tube at 20°:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α.................	−0·61°	−0·59°	−0·59°
[α]...............	−5·58	−5·40	−5·40
[M]	−14·7	−14·2	−14·2

It is seen that in this case also the rotatory dispersion is practically inappreciable.

The optically active acidic sulphonyl derivatives described in the present paper are the only optically active compounds known to possess practically no rotatory dispersion; this, together with the fact that their specific rotatory powers are small compared with those of the corresponding benzoyl derivative, renders them of interest, and it is consequently proposed to study a number of acidic sulphonyl derivatives of other bases in order to ascertain whether the absence of rotatory dispersion is a common characteristic of this class of compounds.

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CLXXX.—*Hydrolysis of Acetic Anhydride.*

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SEVERAL chemists have investigated the reaction of acetic anhydride with water. Menschutkin and Vasilieff (*J. Russ. Phys. Chem. Soc.*, 1889, **21**, 192) studied the change in a homogeneous mixture of acetic acid, anhydride, and water, and showed that the reaction is by no means very rapid. Benrath (*Zeitsch. physikal. Chem.*, 1909, **67**, 501), using molecular proportions of the same three substances, tried to follow the hydrolysis by determining the density. Lumière and Barbier (*Bull. Soc. chim.*, 1906, [iii], **35**, 625), with the aid of Menschutkin and Vasilieff's method, investigated the hydrolysis in 5 and 10 per cent. aqueous solutions of acetic anhydride. Using similar and more dilute aqueous solutions, Rivett and Sidgwick (Trans., 1910, **97**, 733, 1677) followed the hydrolysis by measuring the electric conductivity; their results, which will be discussed further, in general confirm and extend Lumière and Barbier's.

The genesis of our experiments lay in a study of the formation of nitroamines when anilines are treated with nitric acid and acetic anhydride; for this purpose it was necessary to know how rapidly acetic anhydride reacts with water in a medium of glacial acetic acid containing only a fractional percentage of water. The method of estimating acetic anhydride in acetic acid or aqueous acetic acid media, which was discovered by Edwards and Orton (Trans., 1911, **99**, 1181), provided a means of studying the hydrolysis of acetic anhydride in various media, and under the influence of catalysts.

I.—*The Effect of the Medium.*

As media, glacial acetic acid, various aqueous acetic acids, water, aqueous acetone, and acetic anhydride have been used.

Table I shows the effect of the solvent on the rate of hydrolysis. (The composition of the acetic acids is stated by volume.)

TABLE I.

Medium.	Temperature.	Concentration of acetic anhydride.	Velocity-coefficient or velocity-factor.
Glacial acetic acid	16°	0·0804 ($[H_2O]=0·18$)	$k_{II}=0·00042$
97 per cent. acetic acid ...	15	0·081	$k_I=0·0006$
95 ,, ,, ...	16	0·0782	$k_I=0·001$
90 ,, ,, ...	16	0·0815	$k_I=0·0028$
80 ,, ,, ...	16	0·0813	$k_I=0·0056$
50 ,, ,, ...	15	0·083	$k_I=0·016$
Water	15	0·473	$k_I=0·074$
	0	0·495	$k_I=0·028$
95 per cent. aqueous acetone	15	0·087	6 per cent. hydrolysed in 118 hours
50 ,, ,, ,,	15	0·088	$k_I=0·006$
Acetic anhydride	15	$[Ac_2O]=10·3$ $[H_2O]=1·8$	$k_{II}=0·000071$

Obviously, if the hydrolysis of the anhydride is represented by the equation, $Ac_2O+H_2O=2CH_3{\cdot}CO_2H$, the velocity-coefficient, k_{II}, should be given by the equation of the second order. Except in the case of glacial acetic acid and in the last experiment, when the anhydride and water are used alone, the water is in such large excess, and hence of approximately unchanging concentration, that the constant, the velocity factor, $k_I(=k_{II}[H_2O])$, is given by the equation of the first order.

With regard to the media other than water, it is to be noted that acetone provides an environment less favourable to the reaction than acetic acid. In a 50 per cent. aqueous acetone medium the rate is only something more than $\frac{1}{3}$ of a similar aqueous acetic acid medium. In the experiments with an acetic anhydride medium, saturated solutions of water, containing 2·7 grams of water to 100 grams of anhydride, were used. The very small values of the velocity-coefficient show that pure acetic anhydride is a curiously unfavourable medium for its own reaction with water. For aqueous acetic acid media, the speed of hydrolysis is nearly proportional to the concentration of the water; the increase in k_{I} is somewhat more rapid than the increase in the proportion of water.

Hydrolysis in Aqueous Solution.—As is shown in table II, our results in aqueous solution are in agreement with Lumière and Barbier's and Rivett and Sidgwick's.

TABLE II.

Lumière and Barbier.		Rivett and Sidgwick.			Orton and Jones.	
A.	$k_{\mathrm{I}}^{15°}$.	*A.*	$k_{\mathrm{I}}^{25°}$.	$k_{\mathrm{I}}^{15°}$.	*A.*	$k_{\mathrm{I}}^{15°}$.
0·491	0·0735	0·487	0·1383	0·074	0·486	0·074
		0·265	0·1484	0·0793	0·269	0·084
		0·058	0·1561	0·0835		

The velocity factor, k_{I}, has been calculated from the equation $k_{\mathrm{I}} = \frac{1}{t}\log_e\frac{A}{A-x}$, where t is in minutes, A the original concentration of the anhydride in moles per litre, and x the amount changed in time, t. Lumière and Barbier had not deduced a constant from their measurements, which were made at 0° and 15°. Rivett and Sidgwick worked at 25°, using a wide range of concentrations, only the higher of which are suitable for our method of analysis. The values of k_{I} given in the table are not Rivett and Sidgwick's, but those calculated from their numbers by use of the above equation. By taking the ratio, $k_{\mathrm{I}}^{25°}/k_{\mathrm{I}}^{15°} = 1{\cdot}87$, from ours and one of Rivett and Sidgwick's measurements, we have reduced these authors' other values to 15°. Further, by determining k_{I} also at 0°, it has been shown that the value of the velocity factor has the normal relation to temperature.

The most striking fact is that the values of the velocity factor are not independent of the initial concentration of the anhydride, but are larger for the lower concentrations. This relation is given by both Lumière and Barbier's, Rivett and Sidgwick's, and our measurements. Rivett and Sidgwick suggested that this might be partly due to the effect of changing viscosity on their method of measurement, but this peculiarity is not found in the hydrolysis of other anhydrides. Since, however, the relation is still more marked in our values, on which viscosity can have no influence, the value of the velocity factor must actually depend on the initial concentration. It should be noted, however, that the value of k_1 for the lower concentrations continuously falls. We find that measurements made in 50 per cent. acetic acid show the same phenomenon: $A=0{\cdot}0813$, $k_1^{15^\circ}=0{\cdot}0057$; $A=0{\cdot}1625$, $k_1^{15^\circ}=0{\cdot}0047$.

Burke and Donnan (Trans., 1904, **85**, 555) have observed the same phenomenon in the reaction of silver nitrate and alkyl iodides, except that the value of k increases, not decreases, with the initial concentration, and they have shown that it is represented by the exponential law, $k=Kc^n$. By plotting log k for a series of values of c (0·1169—0·3947) against log c from Rivett and Sidgwick's measurements, a straight line is obtained; hence the relation of k to c is expressed by the same law, but the sign of n is negative, since k decreases with concentration.

On the addition of alkalis, hydroxides, carbonates, or hydrogen carbonates, the hydrolysis becomes too fast for measurement. In the presence of acetic acid, Rivett and Sidgwick found a fall in the value of k_1. We have confirmed this fact.

	$[Ac_2O]$.	$[CH_3{\cdot}CO_2H]$.	$[H_2SO_4]$.	$k_1^{15^\circ}$.
Rivett and Sidgwick	0·283 *	—	—	0·079
	0·283	0·828	—	0·0709
Orton and Jones	0·269	—	—	0·084
	0·286	1·0	—	0·07
	0·266	—	0·005*N*	0·09
	0·530	—	0·266*N*	0·11

* Obtained from mean of experiments 21 and 22.

Replacing the acetic acid by an isohydric solution of sulphuric acid, however, produces a rise in the value of k_1.

Sulphuric acid is obviously much less effective than alkalis. With sodium acetate the acceleration is so considerable that the measurements can only be conveniently made at 0°.

In conclusion, it may be said that although hydrogen ions do accelerate hydrolysis in aqueous solution, hydroxyl ions are far more effective, a relation which has been observed in the hydrolysis of esters, and so forth.

II.—*The Effect of Catalysts.*

The effect of acids, sodium acetate, and ferric chloride in acetic acid and aqueous acetic acids has been studied.

? Acids are the most powerful catalysts of the hydrolysis. This effect is most obvious in media containing but little water, and diminishes as the proportion of the water is increased; it is least obvious in pure water.

TABLE III.

Medium.	Concentration of H_2SO_4.	Concentration of Ac_2O.	Temperature.	Speed of hydrolysis.
Glacial acetic acid	—	0·0804	16°	12 per cent. in 24 hrs. $k_{\mathrm{II}}=0{\cdot}00042$
	0·002M	0·077	16	52 per cent. in 10 mins.
97 per cent. acetic acid ...	—	0·081	16	$k_{\mathrm{I}}=0{\cdot}0006$
	0·0041M	0·081	16	$k_{\mathrm{I}}=0{\cdot}0172$
95 ,, ,, ..	—	0·0782	16	$k_{\mathrm{I}}=0{\cdot}001$
	0·004M	0·0813	16	$k_{\mathrm{I}}=0{\cdot}0075$
90 ,, ,, ...	—	0·0815	16	$k_{\mathrm{I}}=0{\cdot}0028$
	0·0166M	0·0807	16	$k_{\mathrm{I}}=0{\cdot}016$
	0·1M	0·091	15	$k_{\mathrm{I}}=0{\cdot}076$
80 ,, ,, ...	—	0·0813	16	$k_{\mathrm{I}}=0{\cdot}0056$
	0·0166M	0·085	15	$k_{\mathrm{I}}=0{\cdot}0084$
50 ,, ,, ...	—	0·083	15	$k_{\mathrm{I}}=0{\cdot}016$
	0·034M	0·0835	15	$k_{\mathrm{I}}=0{\cdot}03$

The acceleration by acids in acetic anhydride or acetone as media is not so great as in glacial acetic acid; thus the hydrolysis has proceeded to the extent of 30 per cent. in nine hours in acetic anhydride, whilst in the presence of a trace of sulphuric acid ($M/794$), 50 per cent. is hydrolysed in four hours. In 95 per cent. acetone, where the hydrolysis is scarcely perceptible, in the presence of the relatively high concentration (0·05M) of hydrochloric acid, the value of the k_{I} is only 0·0011.

Effect of Concentration and Nature of the Acid.—Hydrochloric acid cannot be easily compared with sulphuric acid in glacial acetic acid, owing to the low solubility of the former. In 95 per cent. acetic acid molecular, not equivalent, quantities are found to be equally effective; thus, $k_{\mathrm{I}} = 0{\cdot}0075$ for concentrations of $M/240$ of each acid at 15°. As the medium is further diluted, neither molecular nor equivalent quantities of the acids have an equal effect, but when a medium of 50 per cent. acetic acid is reached, equivalent quantities show the same accelerating effect. Experiments with hydrobromic and perchloric acids demonstrate a similar relation to sulphuric acid.

This relation indicates that we are dealing with the non-ionised acid as effective catalyst in media of 90 per cent. and upwards, and in media of 50 per cent. and below with ionised acids. Measurements of equilibria between hydrochloric acid and chloroamines in various aqueous acetic acid media (Orton and Jones, Trans., 1909, **95**, 1456) lead to identical conclusions. For 90 per cent. and upwards the equilibrium was $\mathrm{NCl}+\mathrm{HCl} \rightleftharpoons :\mathrm{NH}+\mathrm{Cl}_2$, and for 65 per cent. and below: $:\mathrm{NCl}+\mathrm{H}^{\cdot}+\mathrm{Cl}' \rightleftharpoons :\mathrm{NH}+\mathrm{Cl}_2$.

It is not easy to determine the relation between the concentration of the catalyst and the increase of the speed, owing to the limitations imposed by the methods of measurement. In 90 per cent. acetic acid, with sulphuric acid as catalyst, it has, however, been shown that the relation is linear.

TABLE IV.

$[Ac_2O]$.	$[H_2SO_4]$.	$k_I^{15^\circ}$.	$k_I^{15^\circ}/[H_2SO_4]$.
0·0815	—	0·0028	—
0·0795	0·0166M	0·0106	0·66
0·0815	0·033M	0·0196	0·594
0·0823	0·05M	0·035	0·7
0·091	0·1M	0·076	0·76

III.—*Nitric Acid as Catalyst.*

Nitric acid occupies a quite exceptional position. In 50 per cent. acetic acid its catalytic effect on the hydrolysis is identical with that of other acids, but with larger proportions of acetic acid in the medium its relative effectiveness steadily falls, as table V shows, until in glacial acetic acid, when such an acid as sulphuric has greatest influence, that of nitric acid reaches a minimum. Variation of the concentration of nitric acid is shown in the case of 90 per cent. acetic acid medium. It is obviously not linear, as in the case of sulphuric acid.

TABLE V.

Medium.	Catalyst.	Ac_2O.	Temperature.	k_I.
50 per cent. acetic acid ...	—	0·083	15°	0·016
	0·034M-H_2SO_4	0·084	15	0·021
	0·07M-HCl	0·083	15	0·022
	0·071M-HNO_3	0·087	15	0·022
80 ,, ,, ...	—	0·0813	15	0·0057
	0·0165M-H_2SO_4	0·0804	15	0·0084
	0·033M-HCl	0·086	15	0·0139
	0·033M-HNO_3	0·078	15	0·011
90 ,, ,, ...	—	0·0815	15	0·0026
	0·033M-HCl	0·081	15	0·023
	0·0165M-HNO_3	0·083	15	0·0065
	0·033M-HNO_3	0·0805	15	0·008
	0·066M-HNO_3	0·079	15	0·012
95 ,, ,, ...	—	0·078	15	0·001
	0·0041M-HCl	0·083	15	0·007
	0·0166M-HNO_3	0·0857	15	0·0044
Glacial acetic acid............	—	0·0804	15	12 per cent. in 24 hours
	0·002M-H_2SO_4	0·077	15	50 per cent. in 10 minutes
	0·05M-HNO_3	0·088	15	32 per cent. in 24 hours

The great difference between nitric and other acids is not to be attributed to the disappearance of the latter. Solutions of nitric acid in glacial acetic acid have been shown to be quite stable (Orton and Gray, *Analyst*, 1912, **37**, 303), and although in the presence of acetic anhydride there is a slow reduction and disappearance owing to nitration (of the acetic acid or anhydride), it cannot account for its apparent inactivity as a catalyst of hydrolysis; only a few per cent. of the acid is lost in a week.

In solutions where acids are ionised, nitric acid behaves as other acids; the abnormality appears when the acid is not ionised. This singularity is not confined to the hydrolysis of acetic anhydride; whilst a mixture of acetic acid, nitric acid, and acetic anhydride yields nitroaminobenzenes with aniline (Orton, Trans., 1902, **81**, 806), a similar mixture, in which nitric acid is replaced by other acids, is a powerful acetylating agent for anilines, the acid acting as a positive catalyst (Smith and Orton, Trans., 1908, **93**, 1242; 1909, **95**, 1060).

The most obvious suggestion, perhaps, is that the nitric acid combines with the acetic anhydride to form one of the compounds,

$$(CH_3\cdot CO_2)_2N(OH)_3,$$

or acetyl nitrate, $CH_3\cdot CO\cdot O\cdot NO_2$, described by Pictet and Genequand (*Ber.*, 1902, **35**, 2526) and Pictet and Khotinsky (*Ber.*, 1907, **40**, 1163), and hence cannot exert its catalytic effect. Such a suggestion necessitates, in the first place, that these compounds are not much more rapidly hydrolysed than acetic anhydride, and in the second place that they react with the dichloroaniline (in the presence of sodium acetate), forming the acetanilide. But on the supposition that the formation of one or other of these compounds is the cause of the inactivity of nitric acid, certain other properties (such as the hydrolysis into acetic anhydride and nitric acid) must also be attributed to them for the following reasons: The addition of a trace of sulphuric acid to a system containing nitric acid produces its usual powerful effect. Diluting such a system with an equal volume of water leads to the same rate of hydrolysis as is observed when nitric acid is added to acetic anhydride in 50 per cent. acetic acid, that is, the usual acid catalysis. Only further investigation can decide between the various possibilities, and determine the condition which differentiates nitric from other acids.

Discussion of Results.

The results recorded in this paper bring the hydrolysis of acetic anhydride into line with its reactions with hydroxy-compounds and bases, and with the similar hydrolysis of esters, amides, etc. That this would be found to be the case was suggested in the *Annual Reports* (1910, 64) in the discussion of Rivett and Sidgwick's results.

These authors, mainly through the limitations imposed by their method, had been lead to the conclusion that the mechanism of the hydrolysis of acetic anhydride was quite different from that of the hydrolysis of amides and esters (*loc. cit.*, p. 1684). Although acetic anhydride reacts rapidly with most hydroxy- and amino-compounds, the acetylation is greatly accelerated by strong acids, both in the case of hydroxy-compounds (Franchimont, Skraup, and others), and in the case of weak bases (Smith and Orton, *loc. cit.*). A similar relation was therefore to be expected in the reaction with water. In the light of the recent researches of Lapworth, Goldschmidt, and others, mainly on esterification, the following equations may represent the mechanism of the hydrolysis:

(i) $Ac_2O + H_2O = 2AcOH$;
(ii) $Ac_2O + H_2O + H^{\cdot} = 2AcOH + H^{\cdot}$;
(iii) $Ac_2O + H_2O + HX = 2AcOH + HX$;
(iv) $Ac_2O + H_2O + OH' = 2AcOH + OH'$.

The third substance, $H^{\cdot}$, HX, or OH', may be supposed to exert its influence by forming a reacting ionic or non-ionised complex with one or other of the reagents. Any one of the four forms of the hydrolysis may predominate according to the conditions, medium, etc.

In aqueous solution the choice lies between (i), (ii), and (iv). Strong acids have a feeble, whilst bases and even such a slightly hydrolysed salt as sodium acetate have a powerful, catalytic effect. These relations suggest that in aqueous solution hydroxyl ions play the predominant part. In that case traces of acids by decreasing the concentration of the hydroxyl ion should have a great retarding influence. It is true that acetic acid does slightly retard the hydrolysis, but we have not found any such effect with sulphuric. Hence, although hydroxyl ions are powerful catalysts, it may be concluded that in pure water the hydrolysis mainly follows equation (i) and is non-catalytic.

In relatively anhydrous media, reaction (iii) obviously predominates. Molecular quantities of acids are equally effective, and the speed is a linear function of the concentration of the acid.

In media such as 50 per cent. acetic acid or acetone, the catalytic effect is now due to the hydrogen ions (equation ii), for equivalent quantities of acids are of equal influence; but probably here in the absence of strong acids the reaction is also following equation (i).

In media with less than 50 per cent. of water, the catalytic effect of acids follows both equations (ii) and (iii).

EXPERIMENTAL.

The Estimation of Acetic Anhydride.—In order to follow the hydrolysis of acetic anhydride in these experiments, the method of estimating the anhydride devised by Edwards and Orton (*loc. cit.*) has been used. The general procedure is the same as previously described, but for our particular purposes, for example, the estimation of acetic anhydride in aqueous solution, it has been necessary to make some slight modifications. Our procedure is as follows:

The solution of the anhydride which does not contain more than 0·2 gram, is added to a solution of 2:4-dichloroaniline (at least two to three times the quantity equivalent to the anhydride) in so much glacial acetic acid that the final mixture is not below 90 per cent. acetic acid (by volume). Direct trials have shown that the combination of aniline and anhydride is complete in fifteen minutes in 90 per cent. acetic acid, but to a somewhat less extent in 80 per cent. Gentle warming above the water-bath for a short time may be resorted to, and is without any danger of reaction between the acetic acid medium and the aniline.

The anilide is extracted by diluting the mixture to 20 per cent. acetic acid, and shaking with three successive volumes of chloroform. The three volumes of chloroform are shaken vigorously with the solution for three, five, and seven minutes respectively. For every 100 c.c. of diluted solution the three volumes of chloroform are 10, 7, and 3 c.c. It has been found that the first extraction, which contains the larger proportion of the anilide, needs particular care in separating if loss of anilide is to be avoided; the final volume of chloroform only contains 0·92 per cent. of the anilide. The aniline is extracted from the chloroform solution by shaking once for two minutes with 90 c.c. of a 10 per cent. solution of hydrochloric acid for each gram of aniline used. The chloroform solution of the anilide is then mixed with an equal volume of glacial acetic acid and treated with excess of bleaching powder solution to form the chloroamine, $C_6H_3Cl_2{\cdot}NClAc$, such a volume of water being added that the acetic acid aqueous layer is finally 20 per cent. acetic acid (compare Edwards and Orton, *loc. cit.*). After thorough shaking the chloroform is withdrawn, washed with water (containing a little bleaching powder), and evaporated at 30° under slightly diminished pressure in a current of dust-free dry air, which is not drawn from the laboratory, but from the open. This precaution is of importance, as it has been found that the accidental occurrence of reducing gases (hydrogen sulphide and sulphur dioxide) in the laboratory air will often give misleading results by reducing the chloroamine.

The errors in a determination of this type will obviously all be on the negative side, but with practice and scrupulous avoidance of contact of the chloroamine with reducing materials, the error is less than 0·5 per cent.*

In the experiments when aqueous acetone was used as the medium, the aniline was dissolved as before in acetic acid. It was found that acetone retards the interaction of the aniline and anhydride.

When acids were present as catalysts of the hydrolysis, anhydrous sodium acetate at least equivalent to the acid is added to the solution of the aniline before introducing the solution of the anhydride.

Method of carrying out Velocity-measurements.—The acetic acid used was the special material supplied by Kahlbaum and free from reducing substances (Orton, Edwards, and King, Trans., 1911, **99**, 1178). The acetic anhydride was prepared from Kahlbaum's "free from homologues," as described in the following paper.

Our usual procedure in carrying out a measurement is as follows: About 150 c.c. of the medium is brought to the experimental temperature in the bath. When a catalyst is used the requisite quantity dissolved in about 30 c.c. of the medium is placed in the bath. The weighed quantity of the anhydride is placed in a stoppered measuring flask about half filled with the medium; the solution of the catalyst is then added, and the volume made up with the medium (2—5 c.c.) to 100—150 c.c.

At intervals from four to six portions of 10—20 c.c. were with-

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* The following numbers were obtained in testing various stages of the process:

1. Given weights of the chloroamine were dissolved in chloroform, treated with bleaching powder solution, and then the chloroform evaporated.

Chloroamine used.	Chloroamine found.	Loss.
0·1888	0·1882	0·0006=0·3 per cent.
0·2048	0 2046	0·0002=0·1 ,,

2. Given weights of anilide were put through the entire process and estimated as chloroamine.

Anilide used.	Anilide found.	Error.
0·1718	0·1722	+0·2 per cent.
0·1698	0·1703	+0·5 ,,
0·1418	0·1419	
0·2322	0·2321	

3. Given weights of acetic anhydride were treated with aniline and so forth, and estimated as chloroamine.

Anhydride used.	Aniline used.	Anhydride found.	Error.
0·5061	3·0	0·5046	− 0·3 per cent.
0·1828	1·2	0·1820	− 0·6 ,,
0·1564	1·0	0·1560	− 0·2 ,,

drawn and added to the dichloroaniline (and sodium acetate in the case of an acid catalyst) in 10—40 c.c. of acetic acid, that is, such quantity that the medium is 90 per cent. acetic acid. These mixtures were in all cases kept for an hour, but it was often convenient to let them remain overnight. The completion of the analysis of such a series by the method described in the foregoing occupies about four hours.

In the experiments in which a mixture of acetic anhydride and water was used, the anhydride (about 5·59 grams, that is, 5 c.c.) was placed in a weighed flask and brought to the temperature of the bath. A very accurately measured volume of water (about 0·17 c.c.) was then added. At intervals about 0·4 gram was withdrawn and added to the aniline (2 grams) and acetic acid, which had been previously weighed. The increase of weight gives the exact quantity of the mixture withdrawn. When an acid catalyst was used, the acid was dissolved in the water.

In all, something more than three hundred measurements of this kind have been made in the course of this inquiry. No measurement has been accepted unless a coincident duplicate has been obtained.

The following table shows the numbers obtained in typical experiments.

Table VI.

Medium: 97 per cent. acetic acid. Temperature 15°.
Thiosulphate $= 0{\cdot}992N/10$. Exp. 130.

Time (minutes).	C.c. of thiosulphate.	Weight of Ac_2O in 20 c.c.	Percentage changed.	k_1.
0	—	0·1681	0·0	—
160	31·0	0·1570	4·5	0·00059
360	26·5	0·1341	21·2	0·000618
480	24·6	0·1242	26·1	0·00062
595	23·3	0·118	29·8	0·00059
765	20·75	0·105	37·5	0·00061

Medium: 97 per cent. acetic acid. Temperature 16°.
$H_2SO_4 = M/240$. Thiosulphate $= 1{\cdot}047N/10$. Exp. 105.

Time (minutes).	C.c. of thiosulphate.	Weight of Ac_2O in 20 c.c.	Percentage changed.	k_1.
0	—	0·1652	0·0	—
21	20·5	0·1095	33·7	0·0178
33	17·2	0·0918	44·4	0·0178
40	15·4	0·0822	50·2	0·0174
60	10·8	0·0577	65·1	0·0175
72	9·1	0·0486	70·6	0·0168

Medium: 95 per cent. acetic acid. Temperature 16°.
Thiosulphate = 1·23N/10. Exp. 125.

Time (minutes)	C.c. of thiosulphate.	Weight of Ac_2O in 20 c.c.	Percentage changed.	k_{I}.
0	—	0·1657	0·0	—
60	21·8	0·1558	5·8	0·001
210	24·0	0·1505	9·2	0·00102
285	22·75	0·1424	23·6	0·00093
360	20·4	0·1280	31·4	0·00103
465	18·2	0·1142	38·7	0·00105
540	16·7	0·105	44·0	0·00104

Medium: 95 per cent. acetic acid. Temperature 16°.
HNO_3 = N/60. Thiosulphate = 1·047N/10. Exp. 109.

0	—	0·1748	0·0	—
60	27·9	0·149	14·8	0·00266
130	22·8	0·1218	30·3	0·00277
195	18·9	0·1010	42·2	0·0028
270	15·8	0·0844	51·7	0·0027
375	12·25	0·0654	62·6	0·0026
439	10·5	0·0561	67·9	0·0026

Medium: 50 per cent. acetic acid. Temperature 15°.
Thiosulphate = 1·002N/10. Exp. 142.

0	—	0·1695	0·0	—
20·7	23·6	0·1206	29·0	0·0168
31	19·8	0·1012	40·3	0·0166
42·7	16·14	0·0844	50·2	0·0163
50	14·3	0·073	56·9	0·0168
70	10·8	0·0542	68·0	0·0162

Summary.

(1) The hydrolysis of acetic anhydride in glacial acetic acid is a slow reaction of the second order ($k_{\mathrm{II}}^{16^{\circ}}$ = 0·00042). As the acetic acid is diluted, the speed of the hydrolysis increases approximately proportional to the water.

In aqueous acetone, acetic anhydride hydrolyses more slowly than in the corresponding concentrations of acetic acid.

The hydrolysis in solutions of water in acetic anhydride is slower than in acetic acid, thus $k_{\mathrm{II}}^{15^{\circ}}$ = 0·000071.

(2) In aqueous solutions Lumière and Barbier's and Rivett and Sidgwick's results are confirmed. The value of the velocity factor varies with the initial concentration of the anhydride; log k is a linear function of log c for concentrations above 0·115.

The relation of the velocity factor to the temperature is normal.

(3) Acids are very powerful catalysts of the hydrolysis in anhydrous media, but only feeble catalysts in water. Molecular quantities are equally effective in aqueous acetic acid of 90 per

cent. acetic acid and above, but equivalent quantities for 50 per cent. acetic acid and below. The value of the velocity factor is a linear function of the concentration of the acid.

Alkalis and hydrolysed salts are powerful catalysts of the hydrolysis in aqueous solutions.

(4) Nitric acid is unique in its effect. In 50 per cent. acetic acid its effectiveness is equivalent to that of other acids, but as the proportion of the acetic acid in the medium increases, the effectiveness of nitric acid diminishes until in glacial acetic acid it is relatively infinitesimal.

The investigation of the hydrolysis of acid anhydrides and of acylation is being continued.

The authors desire to express their obligation to the Government Grant Committee of the Royal Society and to the British Association for assistance in defraying the cost of this inquiry.

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CLXXXI.—*Acetic Anhydride. The Pure Material, its Physical Properties, and its Reaction with Bromine.*

By Kennedy Joseph Previté Orton and Marian Jones.

For the purposes of the preceding paper, the preparation of pure acetic anhydride was essential. In the literature values for the boiling point ranging from 136·4° to 139·5°/760 mm. are given, with similar divergent values for the density. Pickering (Trans., 1893, **63**, 1000) calls attention to the fact that the separation of acetic acid from acetic anhydride is particularly difficult, and gives the boiling point as 137·4—139·4°. Other authors give similarly wide boiling points for the fractions which they used as acetic anhydride.

The difficulty of testing the purity of acetic anhydride contaminated by acetic acid is due to the want of delicacy in the titration of weighed quantities; thus, 0·51 gram of pure anhydride is equivalent to 100 c.c. $N/10$ $(OH)'$, whilst the same weight of a mixture containing 1 per cent. of acetic acid is equivalent to 99·85 c.c. Menschutkin and Vasilieff's (*J. Russ. Phys. Chem. Soc.*, 1889, **21**, 190) method is more delicate; the anhydride is treated with aniline, and the acetic acid which is produced with the anilide is then titrated; thus, 0·51 gram of anhydride is equivalent to 50 c.c. $N/10$ $(OH)'$, and the same weight of a mixture containing 1 per cent. of acetic acid to 50·35 c.c. In estimating the proportion of acetic acid by this method, however, an error of 0·1 c.c. in the titre is equivalent to an error of 5 per cent. in the amount of acetic acid.

In the method here used (Edwards and Orton, Trans., 1911, **99**, 1181), in which the anhydride is converted into anilide, which is then titrated as chloroamine, the anhydride is directly estimated, and a far greater accuracy is attainable. With the quantities given above, an impurity amounting to 1 per cent. is equivalent to 2 c.c. of $N/20$-thiosulphate, a dilution suitable for this titration.

As the starting point of the purification of the anhydride, Kahlbaum's "Acetic anhydride free from homologues" was used. Most specimens of this material distil completely at a temperature not exceeding 139·5°. With the other commercial anhydrides which we have used, the temperature may rise finally to 142°. In the fractionation of the anhydride, which generally contains as much as 8—10 per cent. of acetic acid, without a still-head, the distillation begins at 134—135°, and only a few per cent. of the anhydride can be obtained of constant boiling point, 139·4°, after repeated fractionation of the fraction of higher boiling point; thus, from 270 c.c. only some 40 c.c. of pure anhydride were isolated. The use of a still-head (the "pear"-form, as described by Young, Trans., 1899, **75**, 679) with eight bulbs leads to a satisfactory separation. Distillation begins at 125°, yielding a liquid which has an odour of acetic acid, and not of anhydride. For the refractionation of the fractions of higher boiling point, the 8-bulb still-head may with advantage be replaced by a 4-bulb. In this way the pure anhydride, amounting to 50—60 per cent. of the original material, can be obtained of constant boiling point, about 139·3—139·4°/760 mm.

The boiling point of the anhydride was determined in an apparatus similar to that used by Thorpe and Rodger, and found to be 139·55°/760 mm.

The specific gravity was determined in a 10 c.c. pyknometer; the mean value was found to be 1·0876 at 15°/4°, and 1·0820 at 20°/4°.

The values given by earlier observers are:

Gerhardt (*Annalen*, 1853, **87**, 149)	138°	at 760 mm.	1·073 at 20·5°
Kopp (*Annalen*, 1855, **93**, 293)	138	,,	1·0792 at 15°/4°
Landolt (*Ann. Phys. Chem.*, 1864, [ii], **122**, 556)	139·25	,,	1·0817 at 20°/4°
Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, *A*, [ii], 516)	139·13	,,	—
Pickering (Trans., 1893, **63**, 1025)	137·7	,,	—
Kahlbaum (*Ber.*, 1883, **16**, 2481)	136·4	,,	—
Vespignani (*Gazzetta*, 1903, **33**, 76)	136·5	,,	1·0797 at 15°/4°
Drucker and Kassel (*Zeitsch. physikal. Chem.*, 1911, **76**, 372)	—		1·0850 at 15°/4°

In the usual books of reference, low values, 136—137°, are generally given, and Landolt's correct numbers are not recorded.

The refractive index has been determined for our pure anhydride by Dr. H. O. Jones. As was to be expected from the fact that Landolt's values for the specific gravity and the boiling point more nearly approach ours than any others, his measurements closely agree with Landolt's. The numbers are for the line H^C.

	Refractive index at 9·5°.	Refractive index at 15°.	Density.
Landolt	1·39317	1·39064	—
Jones	1·39311	1·39069	1·0935 at 9·5°/0° 1·0873 at 15°/0°

The determination of the solubility of water in acetic anhydride can obviously not be made with great accuracy. The appearance of incipient turbidity was easy to observe, and taken as the end-point. One hundred grams of the anhydride dissolve about 2·7 grams of water at 15°. The presence of even small quantities of sulphuric acid reduces the solubility considerably; thus in 100 c.c. of anhydride containing 0·029 gram of sulphuric acid, only 1·8 grams of water will dissolve. The presence of acetic acid in the anhydride greatly increases the solubility of water (0·056 gram of acetic acid will cause an additional 0·03 gram of water to dissolve). Lumière and Barbier (*Bull. Soc. chim.*, 1905, [iii], **33**, 783) state that acetic anhydride is soluble in water approximately to the extent of 12 per cent. at the ordinary temperature.

The Reaction of Acetic Anhydride with Chlorine and Bromine.

In investigating the chlorination and bromination in acetic anhydride solution, we have made a number of experiments on the action of halogens, more especially bromine on pure acetic anhydride.

In the dark, solutions of chlorine and bromine are quite stable, but on exposure to light a reaction occurs. The presence of very small quantities of a number of substances will set up a very rapid reaction; thus it has been found that the acids, sulphuric and perchloric, ferric chloride and iodine, are very effective, but that aluminium chloride, ferric alum, and tin salts have no influence.

The table shows the fall in titre of 5 c.c. of a solution of bromine of about 0·06—0·08 molar concentration in the presence of various reagents. The titre is in c.c. of $N/50$-thiosulphate:

$H_2SO_4 = N/3000$.		$H_2SO_4 = N/2000$.		$H_2SO_4 = N/666$.		$HClO_4 = N/514$.		$I = N/300$.	
t'.	Titre.	t'.	Titre.	t'.	Titre.	t'.	Titre.	t'.	Titre.
0′	12·4	0′	10·5	0′	11·1	0′	8·5	0′	9·4
36	7·35	10	10·15	20·5	6·5	3	7·0	5	9·1
75	4·1	35	8·1	28	4·6	6	4·4	45	2·05
112	2·5	79	4·3	34·5	3·2	11	1·6		

The fall in titre of the bromine bears a linear relation to the time, and hence the fall of titre is independent of the initial concentration of the bromine; for example, in two experiments, using ferric chloride as catalyst, in which the initial concentrations of the bromine were respectively 0·033 and 0·019 moles, a fall of titre of 9 c.c. $N/50$-thiosulphate occurred in 104 and 103 minutes. Lapworth (Trans., 1904, **85**, 30) found exactly the same relation in the action of bromine on acetone, and suggests that it is accounted for by an interaction of bromine with a tautomeride of acetone, which reacts with the bromine far more rapidly than it is produced from acetone.

The rate of fall of titre of the bromine is proportional to the concentration of the catalyst; and, moreover, molecular quantities of perchloric and sulphuric acids are equally effective.

The addition of small quantities of water to the anhydride has a very marked effect in retarding the fall in titre of the bromine in the presence of catalysts. The water, of course, disappears in hydrolysing the anhydride, but the change is sufficiently slow to allow of the former effect being qualitatively observed.

$FeCl_3 = M/535$. Titre of 5 c.c. of Br in c.c. of $N/50$-thiosulphate.

Water, 0 per cent.	t	0	8	12·5	21·5	34 minutes
	Titre ...	10·7	8·7	7·2	4·1	0·1 c.c.
Water, 1 per cent.	t	0	11	33	41	55 minutes
	Titre ...	11·3	9·2	5·1	3·4	0·9 c.c.
Water, 2 per cent.	t	0	20	66	92 minutes	
	Titre ...	10·5	9·9	4·6	2·2 c.c.	

In the presence of water the linear relation no longer holds, the fall of titre now approaching a curve of the logarithmic form.

When iodine is used as catalyst, the behaviour is exceptional, as addition of water increases the rate of disappearance of bromine.

It is to be noted that addition of strong acids in no similar measure accelerates the attack of bromine or chlorine on acetic acid; a solution of bromine containing sulphuric acid at a concentration of $N/6·3$ was found to maintain its titre for several days.

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CLXXXII.—*The Action of Aliphatic Amines on* s-*Dibromosuccinic Acid. Part II. Allylamine.*

By Edward Percy Frankland and Henry Edgar Smith.

By the action of allylamine on *s*-dibromosuccinic acid in ethyl-alcoholic solution, diallylaminosuccinic acid,

$$C_3H_5{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH(CO_2H){\cdot}NH{\cdot}C_3H_5,$$

was obtained in a yield of 68 per cent. When the reaction was carried out in aqueous solution a less pure product was obtained in a yield of only 13 per cent.

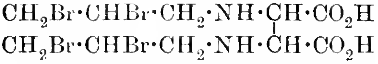
The allylamino-acid possesses properties very similar to those of the dipropylamino- and dibutylamino-succinic acids already described by the authors (this vol., p. 57).

When silver nitrite reacts with the amino-acid monohydrochloride, a mononitroso-derivative of the type

$$R{\cdot}N(NO){\cdot}CH(CO_2H){\cdot}CH(CO_2H){\cdot}NH{\cdot}R$$

is formed, but, unlike in the case of the two above-mentioned alkylamino-acids, the dinitroso-derivative could not be obtained in a pure state by the action of the requisite quantity of nitrous acid derived from either sodium nitrite or silver nitrite.

Diallylaminosuccinic acid combines readily with bromine to form tetrabromodipropylaminosuccinic acid,



$$\begin{array}{l}CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}NH{\cdot}CH{\cdot}CO_2H\\ \qquad\qquad\qquad\qquad\quad\;\; |\\ CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}NH{\cdot}CH{\cdot}CO_2H\end{array}$$

a substance which would appear to offer facilities for the building up of more complex molecules by the replacement of the bromine atoms by amino- or allylamino-groups. Nevertheless, all attempts to produce such compounds proved unsuccessful owing to the unstable character of the parent substance. Indeed, the principal interest attaching to the tetrabromoamino-acid lies in the ease with which it undergoes decomposition. In contrast to the behaviour of other alkylaminosuccinic acids, and of amino-acids in general, one or both bromoalkylamino-groups are readily eliminated from the molecule by heating with acids (concentrated or dilute), and even by water and by alcohol, simultaneous evolution of one molecule of carbon dioxide being also observed. No crystalline products other than salts of *αβ*-dibromopropylamine could be isolated from the reaction mixture. It is noteworthy that tartaric acid does not appear to be an intermediate product in this decomposition, since a quantitative experiment with tartaric acid heated with concentrated hydrochloric acid yielded no carbon dioxide; thus it seems probable that if the bromoalkylamino-groups are replaced by hydroxyl groups there is a preliminary decomposition of the molecule with elimination of carbon dioxide.

We propose to investigate further the properties of brominated alkylamino-compounds with the view of throwing more light on the mechanism of the above reaction, whereby the substituted amino-group may so easily be detached from the acid nucleus.

EXPERIMENTAL.

Action of Allylamine on s-*Dibromosuccinic Acid in* (a) *Ethyl-alcoholic Solution,* (b) *Aqueous Solution.*

Diallylaminosuccinic Acid.

(*a*) A solution of 12 grams of dibromosuccinic acid in 100 c.c. absolute alcohol was treated with 10 grams of allylamine (4 mols.). The solution became warm and deposited the *diallylamine* salt of *dibromosuccinic acid*, which quickly dissolved on heating on the steam-bath. After about forty-five minutes' heating, another substance began to separate out, complete precipitation being obtained after six hours' heating. This substance was collected, washed with alcohol and ether, and, when dry, weighed 6·8 grams. It decomposed at 263—264°.* It was purified by dissolving in the least possible quantity of concentrated hydrochloric acid, and diluting with water, a white powder being immediately precipitated. The mother liquors yielded some allylamine hydrochloride.

Diallylaminosuccinic acid crystallises from aqueous solution in plates, which decompose at 266°. It is insoluble in alcohol or ether, sparingly soluble in hot water, and readily so in concentrated acids or ammonia. The aqueous solution is neutral towards litmus:

0·1935 gave 0·3700 CO_2 and 0·1239 H_2O. $C=52·15$; $H=7·11$.
0·1034 „ 100·53 c.c. CO_2 and 10·27 c.c. N_2.† $C=52·33$; $N=12·48$.
$C_{10}H_{16}O_4N_2$ requires $C=52·63$; $H=7·02$; $N=12·28$ per cent.

(*b*) A solution of 6 grams of dibromosuccinic acid in 50 c.c. of water was treated with 5 grams of allylamine. The amine salt was not deposited as in the previous experiment when alcohol was used as the solvent. The solution was heated on the water-bath for about seven hours, evaporated to dryness, and extracted with water. The insoluble residue weighed 0·65 gram, and decomposed at 258°; it was recrystallised from water containing a small quantity of allylamine, after which it decomposed at 259°.

This substance exhibited properties identical with those of the

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* All melting points uncorrected.

† Dry CO_2 and N_2 at N.T.P.; C and N combustion in a vacuum.

previously described diallylaminosuccinic acid, and gave on analysis the following figures:

0·1207 gave 117·0 c.c. CO_2 and 12·1 c.c. N_2. C=52·19; N=12·60.
$C_{10}H_{16}O_4N_2$ requires C=52·63; N=12·28 per cent.

Monohydrochloride of Diallylaminosuccinic Acid.

A solution of diallylaminosuccinic acid in concentrated hydrochloric acid was evaporated to a small bulk on the water-bath. On stirring the residue with alcohol a white, crystalline powder was deposited. This substance was collected and redissolved in alcohol containing a few drops of hydrochloric acid, from which solution it separated in fine, hexagonal plates melting with decomposition at 176°. It was readily soluble in water, sparingly so in alcohol, and insoluble in ether. The aqueous solution was strongly acid towards litmus:

0·1097 gave 0·0590 AgCl. Cl=13·31.
$C_{10}H_{17}O_4N_2Cl$ requires Cl=13·42 per cent.

Copper Salt of Diallylaminosuccinic Acid.

This compound was prepared in the manner described by the authors in the case of dipropylamino- and dibutylamino-succinic acids (this vol., pp. 60 and 61); it exhibited similar properties to these copper salts, but could not be obtained in a state of purity. The percentage of copper found on analysis was somewhat low, and varied in different preparations (*a* and *b*).

The substance shot up the melting-point tube at 253°, and finally decomposed at 262—263°:

(*a*) 0·4264 gave 0·1088 CuO. Cu=20·37.
0·3817 „ 0·0980 CuO. Cu=20·49.
(*b*) 0·2979 „ 0·0729 CuO. Cu=19·53.
0·1734 „ 0·0426 CuO. Cu=19·61.
$C_{10}H_{14}O_4N_2Cu$ requires Cu=21·95 per cent.

Mononitrosodiallylaminosuccinic Acid.

The previously described diallylaminosuccinic acid monohydrochloride was dissolved in a small volume of water, and the requisite quantity (1 molecule) of silver nitrite added. The reaction mixture was well stirred, and kept cool in ice in a darkened vessel for some hours. The silver chloride was then collected and any slight excess of silver removed from solution by the addition of a drop of dilute hydrochloric acid. The silver-free filtrate, on being evaporated to small bulk over sulphuric acid in a vacuum, deposited a quantity of minute, slender prisms. This was collected, washed with alcohol and with ether, and dried over sulphuric acid in a vacuum.

The substance melted with decomposition at 167° and gave the Liebermann test for a nitroso-compound. It was insoluble in alcohol or ether, sparingly soluble in cold water, the aqueous solution being slightly acid towards litmus:

0·1024 gave 13·35 c.c. N_2. N=16·37.

$C_{10}H_{15}O_5N_3$ requires N=16·34 per cent.

An attempt was made to prepare *dinitrosodiallylaminosuccinic acid* by adding one equivalent of hydrochloric acid to the diamino-acid monohydrochloride, cooling the solution with ice, and adding the requisite quantity of silver nitrite (2 molecules). The reaction mixture was then treated as described above and a white, crystalline substance was obtained, giving the Liebermann test for a nitroso-compound, and melting with vigorous decomposition at 171°. It was sparingly soluble in water and insoluble in alcohol and in ether.

From the result of an analysis, this substance appears to be the mononitroso-derivative.

Found: N=16·03.

$C_{10}H_{15}O_5N_3$ requires N=16·34 per cent.
$C_{10}H_{14}O_6N_4$ „ N=19·58 „ „

Action of Bromine on Diallylaminosuccinic Acid: Tetrabromodipropylaminosuccinic Acid.

11·5 Grams of diallylaminosuccinic acid were dissolved in a small quantity of concentrated hydrobromic acid; the solution was cooled in a freezing mixture and 16·3 grams of bromine (4 molecules), also in concentrated hydrobromic acid, were added slowly with constant stirring.

The solution was then diluted with a large volume of water, whereupon a yellow solid separated out. This substance was collected, washed with alcohol and with ether, and, when dry, weighed 27·5 grams. (Formation of tetrabromodipropylaminosuccinic acid requires 27·63 grams.) If the brominated reaction mixture is heated, a reaction takes place with the formation of $\alpha\beta$-dibromopropylamine hydrobromide (m. p. 164°. Found, C=12·08; N=4·73. $C_3H_8NBr_3$ requires C=12·08; N=4·70 per cent.)

The crude tetrabromodipropylaminosuccinic acid (decomposed 180°) was purified by dissolving it in the least possible quantity of cold concentrated hydrochloric acid and precipitating with water. A white, amorphous solid was obtained, decomposing at 184°, insoluble in cold water and in ordinary organic solvents, readily soluble in cold concentrated acid, and decomposed by acids on heating, as well as by water and by alcohol (see below):

0·2312 gave 94·24 c.c. CO_2 and 9·52 c.c. N_2. C=21·94; N=5·17.
0·1583 „ 0·2158 AgBr. Br=58·01.
$C_{10}H_{16}O_4N_2Br_4$ requires C=21·90; N=5·11; Br=58·39 per cent.

Decomposition of Tetrabromodipropylaminosuccinic Acid with (a) *Hydrochloric Acid,* (b) *Acetic Acid,* (c) *Water,* (d) *Ethyl Alcohol.*

(*a*) 0·8185 Gram of tetrabromodipropylaminosuccinic acid was heated with about 40 c.c. of concentrated hydrochloric acid in a flask immersed in a glycerol bath at about 140°, and the volatile decomposition products aspirated through absorption tubes. The hydrogen chloride was absorbed by a solution of lead nitrate, and the carbon dioxide liberated during the decomposition was dried by passing over sulphuric acid and pumice, and was finally absorbed in weighed tubes containing soda-lime. After heating for two and a-half hours the soda-lime tubes were weighed, and the heating then continued for about four hours longer without further gain in the weight of the soda-lime tubes being observed:

0·8185 gave 0·0664 CO_2. CO_2=8·11.
$C_{10}H_{16}O_4N_2Br_4$ requires CO_2=8·03 per cent. for the elimination of 1 molecule of carbon dioxide.

The reaction mixture was evaporated to dryness on the water-bath and the residue recrystallised from ethyl-alcoholic solution; a substance separated in fine, lenticular crystals (m. p. 163°), which proved to be dibromopropylamine hydrochloride. (Found, Cl=14·46. $C_3H_8NClBr_2$ requires Cl=14·04 per cent.)

The same substance was produced when the tetrabromoamino-acid was heated for half an hour on the steam-bath with a mixture of equal parts of concentrated hydrochloric acid and water, carbon dioxide being also evolved.

(*b*) 1·0 Gram of the tetrabromoamino-acid was heated on the steam-bath with a large volume of glacial acetic acid for forty minutes; the mixture was evaporated to a small bulk and treated with alcohol and animal charcoal. When the alcoholic solution was evaporated an oily liquid remained, which, on treatment with hydrobromic acid, yielded dibromopropylamine hydrobromide (m. p. 162°). The oily liquid was presumably free dibromopropylamine (*Ber.*, 1875, **8**, 399; 1889, **22**, 3076).

(*c*) 6·5 Grams of the tetrabromoamino-acid were heated to boiling with 200 c.c. of water for five hours, the mixture assuming a pale yellow colour during the heating. On collecting the residue it was found that 3·7 grams of the tetrabromoamino-acid had been decomposed, the residue of 2·8 grams having now a decomposition point of 194°. The filtrate was concentrated to a small bulk on the water-bath, under which treatment it darkened considerably, and, on cooling, deposited crystals of dibromopropylamine hydrobromide (m. p. 168°).

Found: Total Br = 80·55.

$C_3H_8NBr_3$ requires Br = 80·54 per cent.

On further concentration the mother liquor yielded a dark, pasty mass, from which no crystalline products could be isolated.

The decomposition with water also resulted in the quantitative elimination of one carboxyl group as carbon dioxide. The apparatus used in this experiment was similar to that described for the hydrochloric acid decomposition, except that the lead nitrate absorption tubes were not used:

2·0036 gave 0·1826 CO_2. CO_2 = 9·11.

$C_{10}H_{16}O_4N_2Br_4$ requires CO_2 = 8·03 per cent. for the elimination of 1 molecule of carbon dioxide.

(*d*) The tetrabromoamino-acid was also decomposed by heating with ethyl alcohol under reflux, 0·6 gram being dissolved by 100 c.c. of alcohol in about seven hours. The alcoholic solution contained ionic bromine.

Thus it would appear that when the tetrabromoamino-acid is heated with either water or alcohol, both dibromopropylamine and hydrogen bromide are produced.

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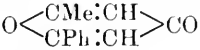
CLXXXIII.—*Studies on Cyclic Ketones. Part I.*

By Siegfried Ruhemann.

In connexion with the work on the formation of cyclic triketones, I have for various reasons subjected the cyclic monoketones to a closer study. In the first place, it was of interest to ascertain whether they behave towards esters of acetylenic acids in a manner similar to the ketonic compounds which contain the ketone group in an open chain. It was previously shown that acetylenic esters combine with β-ketonic esters as well as with β-diketones to form 2-pyrone derivatives (Trans., 1899, **75**, 245, 411), and that they react in the same way with monoketones, in which the group $\cdot CH_2\cdot CO\cdot$ is fixed to electronegative radicles. This is the case with deoxybenzoin, which condenses with ethyl phenylpropiolate to form triphenyl-2-pyrone (Trans., 1910, **97**, 457). The behaviour of the unsaturated ester towards other ketones, for example, acetone, is, however, different, inasmuch as the ester group reacts with one of the methyl radicles of the ketone to yield an acetylenic diketone, thus:

$$(CH_3)_2CO + CO_2Et\cdot C\colon C\cdot C_6H_5 = C_2H_6O + CH_3\cdot CO\cdot CH_2\cdot CO\cdot C\colon C\cdot C_6H_5,$$

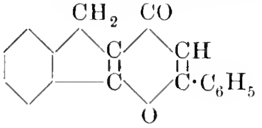
which subsequently condenses to the 4-pyrone,



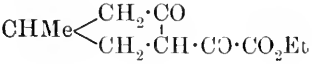
$$O{<}\begin{matrix}CMe\colon CH\\CPh\colon CH\end{matrix}{>}CO$$

(Trans., 1908, **93**, 431, 1281).

It has now been found that ethyl phenylpropiolate, analogously to its condensation with acetone, reacts with the cyclic ketone, α-hydrindone, forming *6-phenyl-2:3-indeno-4-pyrone*,



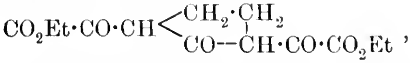
The next object of this work was to apply the action of ethyl oxalate to cyclic ketones, and to use the esters which were expected to be produced for the formation of polycyclic systems, since, up to the present, only ethyl camphoroxalate has been exhaustively studied in this direction (Tingle, *Amer. Chem. J.*, 1900, **23**, 363). Various *cyclo*ketones have, for this purpose, been treated with ethyl oxalate in the presence of sodium ethoxide, and these experiments led to the following results. Whereas *cyclo*pentanone condenses both with one and two molecules of ethyl oxalate, 1-methyl*cyclo*pentan-3-one yields almost exclusively ethyl 1-methyl*cyclo*pentan-3-one-4-oxalate. This behaviour is most probably due to steric hindrance, and points to the formula:



$$CHMe{<}\begin{matrix}CH_2\cdot CO\\ \quad | \\CH_2\cdot CH\cdot CO\cdot CO_2Et\end{matrix}$$

for the ester.

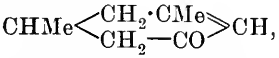
Ethyl cyclo*pentanone-2:5-dioxalate*,



$$CO_2Et\cdot CO\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ \quad | \\CO{-}CH\cdot CO\cdot CO_2Et\end{matrix},$$

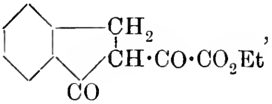
resembles ethyl xanthochelidonate, both in constitution and in properties. Owing to this similarity, attempts have been made to transform the ester into the analogue of chelidonic acid by the method which led Claisen (*Ber.*, 1891, **24**, 111) to the synthesis of chelidonic acid. This task, however, has as yet not been accomplished; in fact, *cyclo*pentanone-2:5-dioxalic acid, which is readily formed on hydrolysis of the ester by alkalis, is stable, and in this respect differs markedly from xanthochelidonic acid.

α-Hydrindone and its methylenedioxy-derivative, as well as 1:3-dimethyl-Δ^3-*cyclo*hexen-5-one,

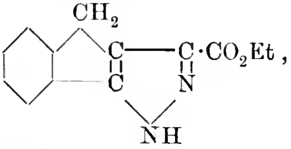


$$CHMe{<}\begin{array}{l}CH_2\cdot CMe\\ CH_2—CO\end{array}{>}CH,$$

in the presence of sodium ethoxide, condense with 1 molecule of ethyl oxalate, and the esters which are produced are readily hydrolysed to the acids. Ethyl 1-hydrindone-2-oxalate,



was subjected to a closer study with the object of transforming it into tricyclic systems; up to the present, the reaction with hydrazine and phenylhydrazine has been investigated. These yield respectively ethyl 4:5-indenopyrazole 3-carboxylate,



and its phenyl derivative.

The action of *p*-nitrosodimethylaniline on cyclic mono- or di-ketones, which led to the knowledge of triketohydrindene hydrate and its methylenedioxy-derivative, has not been lost sight of. It may be mentioned in this connexion that 1:3-dimethyl-Δ^3-*cyclo*hexen-5-one has been investigated in this direction; it was found, however, that it does not yield an azomethine, but that the nitrosodimethylaniline is reduced to *p*-tetramethyldiaminoazoxybenzene,

$$NMe_2\cdot C_6H_4\cdot N_2O\cdot C_6H_4NMe_2.$$

This change, which, in the presence of potassium hydroxide, occurs very readily, is probably accompanied by the oxidation of dimethyl*cyclo*hexenone to *m*-5-xylenol, thus:

$$CHMe{<}\begin{array}{l}CH_2\cdot CMe\\ CH_2—CO\end{array}{>}CH \quad \longrightarrow \quad CMe{<}\begin{array}{l}CH—CMe\\ CH{:}C(OH)\end{array}{>}CH.$$

This view, which it is proposed to subject to experimental test, is supported by the fact that, under the influence of nitrosodimethylaniline and sodium carbonate, ethyl *cyclo*hexane-3:6-dione-

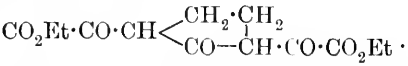
2:5-dicarboxylate (ethyl succinosuccinate) is oxidised to ethyl Δ^1-*cyclo*hexene-3:6-dione-2:5-dicarboxylate, thus:

$$\mathrm{CO}{<}\begin{matrix}\mathrm{CH_2{-}CH(CO_2Et)}\\ \mathrm{CH(CO_2Et){\cdot}CH_2}\end{matrix}{>}\mathrm{CO} \longrightarrow \mathrm{CO}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH(CO_2Et)}\\ \mathrm{C(CO_2Et){=}CH}\end{matrix}{>}\mathrm{CO}.$$

EXPERIMENTAL.

Action of Ethyl Oxalate on cyclo*Pentanone.*

This reaction takes place on gradually adding freshly distilled ethyl oxalate (14·6 grams) to dry sodium ethoxide (6·8 grams) suspended in absolute ether, and then mixing the solution which is produced with *cyclo*pentanone (4·2 grams). A red coloration is developed, and after a short time a jelly is formed, from which a solid gradually separates. The product of the reaction, after being kept for a day, is treated with dilute sulphuric acid, when the colour changes to yellow. The whole is then extracted with much ether, and on evaporation of the ether an oil is left which partly solidifies to a mass of crystals. These are collected with the aid of the pump, freed from the adhering oil by washing with a little ether, and then dissolved in hot alcohol; on cooling, deep yellow plates separate, which melt at 114—115°. This compound is *ethyl* cyclo*pentanone*-2:5-*dioxalate*,



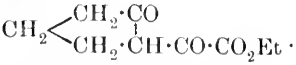
$$\mathrm{CO_2Et{\cdot}CO{\cdot}CH}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CO{-}CH{\cdot}CO{\cdot}CO_2Et}\end{matrix}.$$

0·2105 gave 0·4235 CO_2 and 0·1065 H_2O. C = 54·86; H = 5·62.

$C_{13}H_{16}O_7$ requires C = 54·93; H = 5·63 per cent.

The ester is moderately soluble in ether or cold alcohol, readily so in chloroform or boiling alcohol, and its alcoholic solution gives a deep reddish-brown coloration on the addition of ferric chloride.

The oil which is formed along with this compound contains *ethyl* cyclo*pentanone*-2-*oxalate*,



$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2{\cdot}CO}\\ \mathrm{CH_2{\cdot}CH{\cdot}CO{\cdot}CO_2Et}\end{matrix}.$$

This is isolated by fractionating the oil in a vacuum; first ethyl oxalate, then a pale yellow oil passes over, whilst a small quantity of the dioxalate is left behind. The yellow oil on redistillation boils at 152—153°/15 mm., and in the course of a day sets to a mass of needles, which melt at 26—27°:

0·2015 gave 0·4320 CO_2 and 0·1185 H_2O. C = 58·47; H = 6·53.

$C_9H_{12}O_4$ requires C = 58·69; H = 6·52 per cent.

The alcoholic solution of this ester, like the solution of the former one, gives a deep red coloration on the addition of ferric chloride.

The quantities of the esters which are produced vary, and seem to depend on the temperature. In one experiment, in which the solution formed by the action of ethyl oxalate on sodium ethoxide suspended in ether, was kept cool by running water, whilst *cyclo*pentanone, dissolved in absolute ether, was gradually added, the quantity of the dioxalate which was produced was more than 70 per cent. of the theoretical, whereas it was considerably less, and the yield of the mono-oxalate larger, when the temperature was allowed to rise.

Ethyl *cyclo*pentanone-2:5-dioxalate readily unites with 2 molecules of phenylhydrazine on adding the calculated quantity of the base to an ethereal solution of the ester, when the salt gradually separates on the sides of the vessel in colourless crystals, which are insoluble in ether, and on keeping turn brown:

0·2242 gave 22·c.c. N_2 at 18° and 756 mm. N = 11·27.
$C_{13}H_{16}O_7,2NH_2\cdot NHPh$ requires N = 11·20 per cent.

Ethyl *cyclo*pentanone-2:5-dioxalate dissolves in cold concentrated sulphuric acid to yield a deep yellow solution, from which the ester is precipitated unaltered on the addition of water.

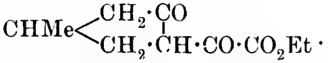
On digesting the ester with dilute potassium hydroxide on the water-bath, the yellow solid first turns red, and then dissolves; after about half an hour the hydrolysis is complete, and the solution yields a yellow, gelatinous precipitate on the addition of an excess of hydrochloric acid. cyclo*Pentanone*-2:5-*dioxalic acid* is almost insoluble in cold water, sparingly so in boiling water, and on cooling separates in groups of yellow needles, which darken at about 195° and melt and evolve gas at 210°:

0·1967 gave 0·3420 CO_2 and 0·0625 H_2O. C = 47·42; H = 3·53.
$C_9H_8O_7$ requires C = 47·37; H = 3·51 per cent.

As mentioned above (p. 1731), the acid could not be transformed into the analogue of chelidonic acid.

Action of Ethyl Oxalate on 1-*Methyl*cyclo*pentan*-3-*one.*

1-Methyl*cyclo*pentan-3-one condenses only with 1 molecule of ethyl oxalate to form ethyl 1-methyl*cyclo*pentan-3-one-4-oxalate,



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2\cdot CH\cdot CO\cdot CO_2Et}\end{matrix}\cdot$$

The reaction takes place under the same conditions as in the former case, and yields an oil which does not deposit a solid product on keeping for several days. After two distillations, a pale yellow oil is obtained, which boils at 150°/14 mm., and gives a deep red coloration on the addition of ferric chloride to its alcoholic solution.

Using 4·9 grams of 1-methyl*cyclo*pentan-3-one, the yield of the pure ester is 6—7 grams:

0·2195 gave 0·4870 CO_2 and 0·1375 H_2O. C = 60·50; H = 6·96.
$C_{10}H_{14}O_4$ requires C = 60·60; H = 7·07 per cent.

Ethyl 1:3-*Dimethyl*-Δ^3-cyclo*hexen*-5-*one*-6-*oxalate*,

$$\mathrm{CMe}\Big\langle\begin{matrix}\mathrm{CH_2\cdot CHMe}\\ \mathrm{CH{-\!-\!-}CO}\end{matrix}\Big\rangle\mathrm{CH\cdot CO\cdot CO_2Et.}$$

On adding 1:3-dimethyl-Δ^3-*cyclo*hexen-5-one (6·2 grams) to the solution which is formed by the action of ethyl oxalate (7·5 grams) on dry sodium ethoxide (3·4 grams) suspended in absolute ether, a yellow solid is produced. The product of the reaction is kept overnight, and then treated in the usual way, when a yellow oil is obtained which gradually sets to a semi-solid mass of crystals. These are collected, freed from the adhering dark oil by placing them on a porous plate, and recrystallised from dilute alcohol. Yellow needles are obtained, which melt at 132—133°:

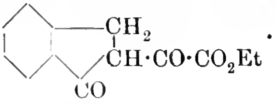
0·2020 gave 0·4765 CO_2 and 0·1300 H_2O. C = 64·33; H = 7·15.
$C_{12}H_{16}O_4$ requires C = 64·29; H = 7·14 per cent.

The ester is readily soluble in alcohol, and this solution gives a deep brown coloration on the addition of ferric chloride.

1:3-*Dimethyl*-Δ^3-cyclo*hexen*-5-*one*-6-*oxalic Acid*.—The ester dissolves in cold dilute potassium hydroxide; on digesting the solution for a short time on the water-bath, hydrolysis takes place, and the acid is precipitated on the addition of dilute hydrochloric acid to the alkaline liquor as a pale yellow solid. This is moderately soluble in boiling water, readily so in alcohol, and crystallises from the aqueous solution in yellow prisms distinctly less coloured than the ester. It softens at 170°, and melts and decomposes at 178°:

0·2015 gave 0·4530 CO_2 and 0·1125 H_2O. C = 61·31; H = 6·20.
$C_{10}H_{12}O_4$ requires C = 61·22; H = 6·12 per cent.

Ethyl 1-*Hydrindone*-2-*oxalate*,



This ester is readily formed on adding α-hydrindone (6·6 grams), dissolved in absolute ether, to the solution which is produced by the action of ethyl oxalate (7·4 grams) on dry sodium ethoxide (3·4 grams) suspended in ether. The mixture, which immediately deposits a yellow solid, is kept overnight, then treated with an excess of dilute sulphuric acid, and extracted with ether. On evaporation of the ether an oil is left, which soon sets to a solid. This is very soluble in hot alcohol, and, on cooling the concentrated solution, crystallises in colourless needles, which melt at 74—75°:

0·2030 gave 0·5010 CO_2 and 0·0945 H_2O. C=67·30; H=5·17.
$C_{13}H_{12}O_4$ requires C=67·24; H=5·17 per cent.

The alcoholic solution of the ester gives a dark brown coloration with ferric chloride. On mixing the ethereal solution of the ester with phenylhydrazine, the salt, $C_{13}H_{12}O_4,NH_2{\cdot}NH{\cdot}C_6H_5$, separates in colourless crystals:

0·2365 gave 17·2 c.c. N_2 at 18° and 759 mm. N=8·38.
$C_{13}H_{12}O_4,NH_2{\cdot}NHPh$ requires N=8·24 per cent.

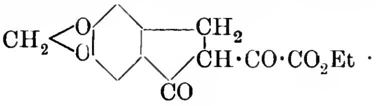
The salt turns yellow in the course of a few days, and loses phenylhydrazine when heated in the steam-oven.

1-*Hydrindone-2-oxalic Acid.*—On digesting the ester with dilute potassium hydroxide, it first develops a deep yellow colour and then dissolves, forming a colourless solution, which, with hydrochloric acid, yields a gelatinous precipitate. This is sparingly soluble in boiling water, moderately so in hot ethyl acetate or alcohol, and crystallises from these solutions in faintly yellow needles, which soften at 210°, and melt and decompose at 214°:

0·2165 gave 0·5130 CO_2 and 0·0795 H_2O. C=64·62; H=4·08.
$C_{11}H_8O_4$ requires C=64·70; H=3·92 per cent.

The acid dissolves in cold concentrated sulphuric acid to form a yellow solution, from which the ketonic acid is precipitated unaltered on the addition of water.

5:6-*Methylenedioxy*-1-*hydrindone*-2-*oxalic Acid*,

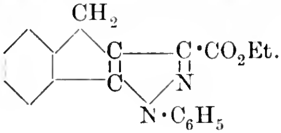


Owing to the fact that 5:6-methylenedioxy-1-hydrindone is not readily soluble in ether, dry benzene must be used as a solvent. The hot solution of the ketone is mixed with the product of the reaction between ethyl oxalate and sodium ethoxide, suspended in benzene; after three hours' digestion on the water-bath, dilute hydrochloric acid is added, and the precipitate is collected. This product is a mixture of the unaltered hydrindone and ethyl 5:6-methylenedioxy-1-hydrindone-2-oxalate, which could not be separated by fractional crystallisation. The separation, however, can be effected by digesting the mixture with dilute potassium hydroxide on the water-bath, when the ester is hydrolysed. On adding dilute hydrochloric acid to the alkaline filtrate from the unchanged 5:6-methylenedioxy-1-hydrindone, the ketonic acid is precipitated as a gelatinous solid. It dissolves in much boiling water, and, on cooling, the solution gradually separates as a yellow powder consisting of aggregates of needles, which soften at 255°, and melt and decompose at 260°:

0·2045 gave 0·4353 CO_2 and 0·0612 H_2O. C=58·05; H=3·32.
$C_{12}H_8O_6$ requires C=58·06; H=3·23 per cent.

The acid is sparingly soluble in boiling alcohol, and the solution gives a deep reddish-brown coloration with ferric chloride.

Ethyl 1-*Phenyl*-4:5-*indenopyrazole*-3-*carboxylate*,



Whereas ethyl 1-hydrindone-2-oxalate, dissolved in ether, reacts with phenylhydrazine to form a salt of the ester, it yields *ethyl* 1-*phenyl*-4:5-*indenopyrazole*-3-*carboxylate* if its concentrated alcoholic solution is digested with phenylhydrazine hydrochloride in the presence of a little hydrochloric acid for about half an hour on the water-bath. On cooling, slightly coloured crystals separate, which on recrystallisation from dilute alcohol are obtained in pale yellow needles melting at 117—118°:

0·2083 gave 0·5715 CO_2 and 0·0985 H_2O. C=74·83; H=5·27.
0·2540 „ 20·8 c.c. N_2 at 20° and 760 mm. N=9·37.
$C_{19}H_{16}O_2N_2$ requires C=75·0; H=5·26; N=9·21 per cent.

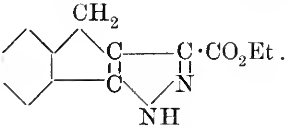
The ester is readily soluble in alcohol, and the alcoholic solution does not gives a coloration with ferric chloride. The compound is hydrolysed by digesting its solution in alcohol with alcoholic potassium hydroxide on the water-bath; at first a red coloration develops, which rapidly disappears, and at the same time the whole sets to a white, semi-solid mass. After evaporation of the alcohol, the product is dissolved in water, and the solution treated with dilute hydrochloric acid, when 1-*phenyl*-4:5-*indenopyrazole*-3-*carboxylic acid* is precipitated as a white solid. As this can be collected by filtration only with difficulty, it was found convenient to dissolve it in ether, of which a large volume is required. The solid which is left on distillation of the ether, is only sparingly soluble in benzene, moderately so in ether, but readily so in hot dilute alcohol, and on cooling crystallises in almost colourless needles, which melt and decompose at 250—251°:

0·1530 gave 0·4133 CO_2 and 0·0605 H_2O. C=73·67; H=4·39.
0·2140 „ 19·2 c.c. N_2 at 19° and 760 mm. N=10·31.
$C_{17}H_{12}O_2N_2$ requires C=73·91; H=4·35; N=10·14 per cent.

The acid is also formed on adding an aqueous solution of phenylhydrazine hydrochloride, containing a little free hydrochloric acid, to 1-hydrindone-2-oxalic acid dissolved in boiling water (of which a large quantity is required), when 1-phenyl-4:5-indenophenylpyrazole-3-carboxylic acid separates as a white powder. The acid dissolves in ammonia on warming, and the solution, on the addition of silver nitrate, gives a *silver* salt, which is gelatinous, but on heating becomes curdy, and can then be collected; it is insoluble in water, and not attacked by light:

0·2450 gave 0·0690 Ag. Ag=28·16.
$C_{17}H_{11}O_2N_2Ag$ requires Ag=28·20 per cent.

Ethyl 4:5-*Indenopyrazole*-3-*carboxylate*,



This compound is formed in a similar manner to the former ester, namely, by treating ethyl 1-hydrindone-2-oxalate, dissolved in alcohol, with an aqueous solution of hydrazine hydrochloride containing a little hydrochloric acid. The mixture turns red, and, on cooling, colourless prisms separate, which, after recrystallisation from alcohol, melt at 174°:

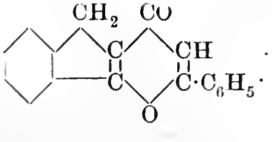
0·2065 gave 0·5175 CO_2 and 0·0970 H_2O. C=68·35; H=5·22.
$C_{13}H_{12}O_2N_2$ requires C=68·42; H=5·26 per cent.

4:5-*Indenopyrazole*-3-*carboxylic acid* is formed from the ester on hydrolysis with alcoholic potassium hydroxide. It is a white, crystalline substance, which is almost insoluble in all organic solvents, and dissolves only sparingly in boiling water; it melts and decomposes at 310°, after having darkened at a somewhat lower temperature:

0·2070 gave 25·4 c.c. N_2 at 22° and 762 mm. N=13·92.
$C_{11}H_8O_2N_2$ requires N=14·0 per cent.

Action of Ethyl Phenylpropiolate on α-Hydrindone.

This reaction, which yields 6-phenyl-2:3-indeno-4-pyrone,



takes place on adding α-hydrindone (6·6 grams) to dry sodium ethoxide (3·4 grams) suspended in absolute ether, and then ethyl phenylpropiolate (8·7 grams). The mixture, which becomes deep brown, is kept for two to three days, then treated with dilute hydrochloric acid, and extracted with ether. The ethereal solution is washed with sodium carbonate, and on evaporation of the ether yields a solid, together with a dark-coloured, viscous oil. The latter can be removed by washing the product with ether and pressing it between filter paper. The solid which remains readily dissolves in hot alcohol, and, on cooling, yellow needles separate, which, after repeated crystallisations from dilute alcohol, are obtained almost colourless, and then melt at 169°. The substance contains 1 molecule of water of crystallisation, which it loses very slowly in a vacuum desiccator over sulphuric acid, but readily on drying in the steam-oven; at the same time the crystals lose their lustre and become opaque:

0·2172 * at 100° lost 0·0142. $H_2O = 6·54$.

$C_{18}H_{12}O_2,H_2O$ requires $H_2O = 6·47$ per cent.

0·2030 † gave 0·6182 CO_2 and 0·0855 H_2O. C = 83·05; H = 4·67.

$C_{18}H_{12}O_2$ requires C = 83·08; H = 4·61 per cent.

6-*Phenyl*-2:3-*indeno*-4-*pyrone* is insoluble in water, and, when pure, only sparingly soluble in ether or light petroleum, but readily so in alcohol; it does not dissolve in potassium hydroxide, and is scarcely attacked by it, even on boiling. The compound forms a *platinichloride*, which separates in yellow plates on adding to the alcoholic solution of the pyrone hydrochloric acid and concentrated platinic chloride. For analysis it was washed with alcohol and dried in the steam-oven:

0·2875 gave 0·0600 Pt. Pt = 20·87.

$(C_{18}H_{12}O_2)_2,H_2PtCl_6$ requires Pt = 20·92 per cent.

Action of p-*Nitrosodimethylaniline on* 1:3-*Dimethyl*-Δ³-cyclo-*hexen*-5-*one*.

Sachs' method of transforming methylene groups into ketonic groups, which led to the formation of triketohydrindene hydrate and its methylenedioxy-derivative, has since been applied to other cyclic ketones with the object of preparing polyketonic compounds and studying their chemical behaviour. It was found, however, that nitrosodimethylaniline acts on certain members of this class of substances as an oxidising agent, instead of yielding azomethines. This is the case with 1:3-dimethyl-Δ³-*cyclo*hexen-5-one. On adding a little concentrated alcoholic potassium hydroxide to

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* Air-dried. † Dried at 100°.

the mixture of the ketone and the base dissolved in alcohol, heat is developed, and a dark solid immediately separates, which crystallises from alcohol in brown prisms. The melting point (242°) and the analysis (Found, $C=67\cdot61$; $H=7\cdot06$. Calc., $C=67\cdot60$; $H=7\cdot04$) characterise the compound as *p*-tetramethyldiaminoazoxybenzene, $NMe_2\cdot C_6H_4\cdot N_2O\cdot C_6H_4NMe_2$. Its formation is probably accompanied by the oxidation of 1:3-dimethyl-Δ^3-*cyclo*hexen-5-one to *m*-5-xylenol. This view is supported by the result of the following experiment.

Action of p-*Nitrosodimethylaniline on Ethyl* cyclo*Hexane-3:6-dione-2:5-dicarboxylate (Ethyl Succinosuccinate).*

On boiling a mixture of the ester (4 grams) and *p*-nitrosodimethylaniline (5 grams) dissolved in alcohol with a small quantity of concentrated sodium carbonate for a few minutes, the solution darkens and deposits a yellow solid (2·5 grams). This dissolves in hot alcohol, and, on cooling, crystallises in yellow prisms. The substance was identified with ethyl Δ'-*cyclo*hexene-3:6-dione-2:5-dicarboxylate by the melting point (133—134°) and the deep bluish-green coloration which its alcoholic solution gives with ferric chloride.

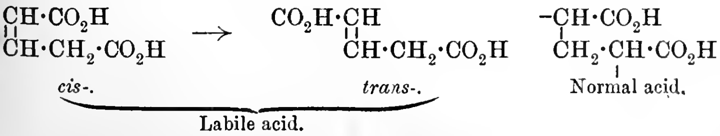
In conclusion, I have great pleasure in acknowledging my indebtedness to the Farbwerke vorm. F. Bayer & Co., and especially to Dr. F. Hofmann, Director of the Pharmaceutical Department of the works, for their kindness in supplying me with a quantity of valuable material which enabled me to carry out this research.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CLXXXIV.—*The Chemistry of the Glutaconic Acids. Part VI. Conditions which Confer Stability on the* trans-*Forms of the Labile Acids.*

By NORMAN BLAND and JOCELYN FIELD THORPE.

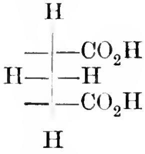
THE experimental evidence already published points to the conclusion that, although the labile form of an acid of the glutaconic series should theoretically exist in *cis*- and *trans*-modifications, thus:



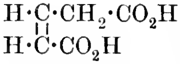
$$\underbrace{\underset{cis\text{-.}}{\begin{array}{l}\text{CH}\cdot\text{CO}_2\text{H}\\ \|\\ \text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}\end{array}} \longrightarrow \underset{trans\text{-.}}{\begin{array}{l}\text{CO}_2\text{H}\cdot\text{CH}\\ \qquad\quad\;\;\|\\ \qquad\quad\;\;\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}\end{array}}}_{\text{Labile acid.}} \qquad \underset{\text{Normal acid.}}{\begin{array}{l}-\text{CH}\cdot\text{CO}_2\text{H}\\ \;\;|\\ \;\;\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}\\ \qquad\quad\;\;|\end{array}}$$

the isolation of such forms cannot be effected in the case of the simpler members of the series, owing to the fact that the greater stability of the normal state causes the production of this modification in all reactions which should convert the *cis*-labile acid into its *trans*-isomeride.

It is evident that both the normal and labile forms of the acids isolated up to the present time have the *cis*-configuration; that is to say, both states have the carboxyl groups on the same sides of the terminal tetrahedrons, thus:



Normal acid.

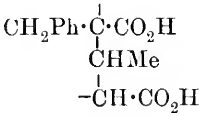


$$\begin{array}{l} H\cdot C\cdot CH_2\cdot CO_2H \\ \;\;\,\| \\ H\cdot C\cdot CO_2H \end{array}$$

Labile acid.

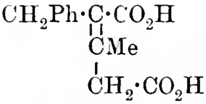
a conclusion which follows, not only because both acids are formed by the hydration of the anhydride, but also from the fact that both modifications yield the hydroxy-anhydride with equal readiness.

It is therefore reasonable to assume that the *trans*-forms of the labile acids could only be isolated in those cases in which the labile acids themselves possess great stability, and since it has been shown that this stability increases with the weight of the group attached to one of the terminal carbon atoms of the three-carbon system, and is greatly enhanced by the presence of a methyl group on the central carbon atom of the system, it was decided to prepare α-benzyl-β-methylglutaconic acid:



$$\begin{array}{l} CH_2Ph\cdot \overset{|}{C}\cdot CO_2H \\ \qquad\quad | \\ \qquad\;\; CHMe \\ \qquad\quad | \\ \quad\;\; -CH\cdot CO_2H \end{array}$$

Normal form.



$$\begin{array}{l} CH_2Ph\cdot C\cdot CO_2H \\ \qquad\quad \| \\ \qquad\;\; CMe \\ \qquad\quad | \\ \qquad\;\; CH_2\cdot CO_2H \end{array}$$

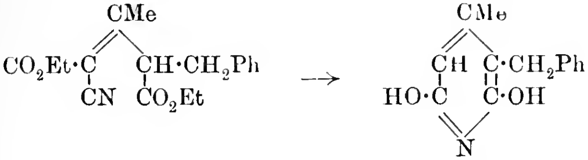
Labile form.

and to subject it to a thorough investigation.

The preparation of the acid was, in the first instance, effected by the hydrolysis of the ester (I), which can be prepared by the action of benzyl chloride on the potassium compound (II) (compare this vol., p. 889):

$CO_2Et\cdot C(CN){:}CMe\cdot CHK\cdot CO_2Et + PhCH_2Cl \longrightarrow$
(II.)
$CO_2Et\cdot C(CN){:}CMe\cdot CH(CH_2Ph)\cdot CO_2Et + KCl$
(I.)

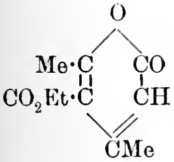
and in this way a small yield of the normal acid, melting at 148°, was obtained, using hydrochloric acid as the hydrolysing agent. It was at once evident, however, that this method could not be used for the production of large quantities of the acid, and, moreover, it was found that the action of alkalis could not be employed for the purpose of hydrolysis, since, like similar substances of this type (Trans., 1905, **87**, 1699), the cyano-ester is converted into the stable dihydroxypyridine derivative (III) under these conditions:



(III.)
M. p. 176°.

The conditions, therefore, most favourable for the production of the labile acid could not be used.

It was in this connexion that the method ultimately used for the isolation of the labile modifications of the acids described in Part V (this vol., p. 1557) was devised, that is to say, the labile ester of the above benzyl methyl acid was prepared by the action of benzyl chloride on the sodium derivative formed by the action of sodium ethoxide on ethyl *iso*dehydracetate, thus:



$+ NaOEt + PhCH_2Cl + EtOH \longrightarrow$

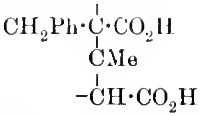
$CO_2Et{\cdot}C(CH_2Ph){:}CMe{\cdot}CH_2{\cdot}CO_2Et + CH_3{\cdot}CO_2Et + NaCl.$

and in this way a good yield of ester was obtained, from which the labile acid was prepared by the action of alkalis, and from which the normal acid was produced by hydrolysis with acids.

It was at once evident that the labile acid prepared in this manner possessed properties very different from those shown by the other member of the series; thus, whereas in all the cases previously investigated there was no essential difference between the normal and labile forms in respect of their capacity for anhydride-formation, the normal and labile states of α-benzyl-β-methylglutaconic acid show a marked difference; thus the normal acid eliminates water-vapour almost immediately after melting, whereas the labile acid melts without decomposition, and does not evolve gas unless heated at 200°.

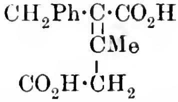
A similar difference is shown in the behaviour of the two acids towards acetyl chloride, for whereas the normal acid yields the hydroxy-anhydride when treated with the cold reagent, the labile acid requires to be heated for some time before anhydride-formation is complete.

We have therefore arrived at the conclusion that the labile acid formed in this manner has the *trans*-configuration, and that the two acids mentioned above have the formulæ:



$$\begin{array}{c} | \\ \mathrm{CH_2Ph{\cdot}C{\cdot}CO_2H} \\ | \\ \mathrm{CMe} \\ | \\ \mathrm{-CH{\cdot}CO_2H} \end{array}$$

(Normal acid, m. p. 148°.)



$$\begin{array}{c} \mathrm{CH_2Ph{\cdot}C{\cdot}CO_2H} \\ \| \\ \mathrm{CMe} \\ | \\ \mathrm{CO_2H{\cdot}CH_2} \end{array}$$

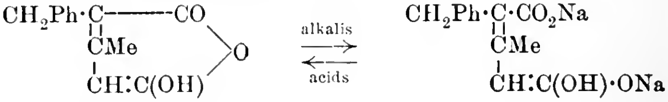
(*trans*-Labile acid, m. p. 134°.)

It was therefore necessary to search for the *cis*-modification of the labile acid, but ultimately we were forced to the conclusion that this acid, like the corresponding modification of β-phenylglutaconic acid (this vol., p. 860), is unstable, and passes into the hydroxy-anhydride when any attempt is made to liberate it from its salts; this conclusion is based on the following experiments:

(1) The hydroxy-anhydride passes into the normal acid when treated with water, but when hydrolysed by dilute alkali in the presence of casein the hydroxy-anhydride is regenerated.

(2) When the hydroxy-anhydride is dissolved in excess of concentrated aqueous alkali, the oily alkali salt is precipitated. This salt is insoluble in concentrated aqueous alkali, but slowly passes into solution on keeping. The clear solution, which cannot contain any unchanged salt of the hydroxy-anhydride deposits, when acidified, an amount of the anhydride corresponding with about half the weight of acid used in the experiment, whilst the filtrate on cautious treatment with hydrochloric acid yields the *trans*-form of the labile acid.

It is probable that the true explanation of this behaviour is to be traced to the great stability of the enolic form of the labile state which has been shown to be conferred on compounds of this type by the entrance of heavy groups on the carbon atoms of the three-carbon system, and that actually the *cis*-form is incapable of isolation. In other words, the salt formed by the fission of the pyrone ring by alkali in all probability retains the hydrogen atom on the oxygen of the carbonyl system, thus:



$$\begin{array}{c} \mathrm{CH_2Ph{\cdot}C\text{———}CO} \\ \| \qquad\qquad \diagdown \\ \mathrm{CMe} \qquad\qquad \mathrm{O} \\ | \qquad\qquad \diagup \\ \mathrm{CH{:}C(OH)} \end{array} \underset{\text{acids}}{\overset{\text{alkalis}}{\rightleftarrows}} \begin{array}{c} \mathrm{CH_2Ph{\cdot}C{\cdot}CO_2Na} \\ \| \\ \mathrm{CMe} \\ | \\ \mathrm{CH{:}C(OH){\cdot}ONa} \end{array}$$

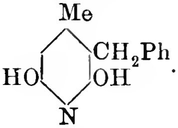
Hydroxy-anhydride,
m. p. 69°.

The *trans*-form of the labile acid differs from the normal acid in forming a soluble barium salt. It is very sensitive towards mineral acids, especially when it is liberated from its salts by this means;

when once isolated it is a comparatively stable substance, but is partly converted into the normal acid when boiled with dilute mineral acid.

Experimental.

2:6-*Dihydroxy-3-benzyl-4-methylpyridine*,



This substance is the sole product when normal ethyl α-cyano-γ-benzyl-β-methylglutaconate (this vol., p. 889) is heated with an alcoholic solution of twice the calculated quantity of potassium hydroxide until completely hydrolysed. The pyridine derivative, isolated in the usual manner, crystallises from alcohol in small needles, which melt at 176°:

0·1533 gave 0·4058 CO_2 and 0·0857 H_2O. C=72·21; H=6·21.
$C_{13}H_{13}O_2N$ requires C=72·6; H=6·0 per cent.

The compound gives an intense wine-red coloration with ferric chloride in alcoholic solution, and yields an oily hydrochloride with concentrated hydrochloric acid, from which the base is regenerated by the action of water. It is soluble in aqueous alkaline carbonates.

The *dibenzoyl* derivative prepared by the Schotten-Baumann method crystallises from alcohol in prisms, which melt at 133°:

0·1865 gave 0·5224 CO_2 and 0·0880 H_2O. C=76·38; H=5·24.
$C_{27}H_{21}O_4N$ requires C=76·60; H=5·0 per cent.

When ethyl α-cyano-γ-benzyl-β-methylglutaconate is hydrolysed with dilute hydrochloric acid, a small quantity of acid can be isolated from the dihydroxypyridine derivative, which is the chief product. The acid melts at 148°, and is evidently normal α-benzyl-β-methylglutaconic acid, the properties of which are described later in the paper.

Labile Ethyl α-Benzyl-β-methylglutaconate,
$CO_2Et{\cdot}C(CH_2Ph){:}CMe{\cdot}CH_2{\cdot}CO_2Et$.

In order to prepare this substance, 60 grams of ethyl *iso*dehydracetate, diluted with an equal volume of alcohol, were added to a solution of 6·9 grams of sodium in 85 grams of alcohol at −5°. The deep yellow solution was kept at 0° for fifteen minutes, and then cautiously mixed with excess of benzyl chloride, care being taken to prevent any appreciable rise of temperature. After the mixture had remained for one hour, the reaction was completed by warming on the water-bath, and the product isolated by removing the alcohol and unchanged benzyl chloride by distillation in a current of steam and extracting the non-volatile oil by ether.

The ester is a moderately viscid oil, which distils at 195°/20 mm.:

0·1822 gave 0·4726 CO_2 and 0·1237 H_2O. C=70·71; H=7·54.

$C_{17}H_{22}O_4$ requires C=70·4; H=7·6 per cent.

The ester gives no coloration with ferric chloride, and is not extracted from its solution in ether by aqueous alkali.

Normal α-*Benzyl*-β-*methylglutaconic Acid*,

$CO_2H\cdot\underset{\cdot}{C}(CH_2Ph)\cdot CHMe\cdot\underset{\cdot}{C}H\cdot CO_2H$.

The hydrolysis of labile ethyl α-benzyl-β-methylglutaconate by 10 per cent. aqueous hydrochloric acid proceeds very slowly, and after boiling for two days some ester remains unaltered. The acid can be extracted from the ethereal solution of the product by aqueous sodium carbonate, and is precipitated as an oil on acidifying the alkaline extract. The acid prepared in this manner contains some of the labile modification, from which it may be separated by means of its *barium* salt, which separates in the crystalline form when a solution of the ammonium salt and barium chloride is boiled:

0·2911 gave 0·1804 $BaSO_4$. Ba=36·84.

$C_{13}H_{12}O_4Ba$ requires Ba=37·12 per cent.

The normal acid obtained from the barium salt by hydrochloric acid crystallises from dilute alcohol in slender needles, which melt at 148° with immediate elimination of gas:

0·1663 gave 0·4051 CO_2 and 0·0929 H_2O. C=66·43; H=6·20.

$C_{13}H_{14}O_4$ requires C=66·7; H=6·0 per cent.

The pure acid is insoluble in hot benzene.

The *silver* salt is a white, crystalline precipitate:

0·2773 gave 0·1334 Ag. Ag=48·10.

$C_{13}H_{12}O_4Ag_2$ requires Ag=48·21 per cent.

The soluble barium salt from the above separation yielded a small quantity of the acid of lower melting point (see below).

Normal Ethyl α-*Benzyl*-β-*methylglutaconate*,

$CO_2Et\cdot\underset{\cdot}{C}(CH_2Ph)\cdot CHMe\cdot\underset{\cdot}{C}H\cdot CO_2Et$.

This ester is formed by the etherification of the normal acid by alcohol and sulphuric acid in the usual manner. It boils at 193°/18 mm., and is similar to the labile ester in appearance:

0·1859 gave 0·4791 CO_2 and 0·1271 H_2O. C=70·28; H=7·60.

$C_{17}H_{22}O_4$ requires C=70·4; H=7·6 per cent.

The structure of this substance is evident from the fact that it yields the normal acid under the same conditions of alkaline hydrolysis as those which transform the labile ester into the labile acid.

Labile trans-*α-Benzyl-β-methylglutaconic Acid*, $CO_2H\cdot C(CH_2Ph)\colon CMe\cdot CH_2\cdot CO_2H$.

This acid is produced by the hydrolysis of the labile ester with twice the calculated quantity of potassium hydroxide dissolved in alcohol, and can be isolated in the usual manner. It separates from benzene in small, flattened needles, which melt at 134°, and eliminate gas at 200°:

0·1814 gave 0·4445 CO_2 and 0·0971 H_2O. C=66·83; H=5·95.

$C_{13}H_{14}O_4$ requires C=66·7; H=6·0 per cent.

The acid can be distinguished from its normal isomeride by its solubility in benzene, and by the formation of soluble salts with calcium and barium.

The *silver* salt is a white, crystalline powder:

0·2719 gave 0·1309 Ag. Ag=48·13.

$C_{13}H_{12}O_4Ag_2$ requires Ag=48·21 per cent.

The Hydroxy-anhydride of α-Benzyl-β-methylglutaconic Acid (*6-Hydroxy-3-benzyl-4-methyl-α-pyrone*),

$$CMe<\begin{matrix}C(CH_2Ph)\cdot CO\\ CH{=\!=}C(OH)\end{matrix}>O.$$

Both the normal and labile acids pass into the hydroxy-anhydride when heated on the water-bath with ten times the weight of acetyl chloride, but whereas the former requires to be heated for a quarter of an hour, the reaction in the case of the labile acid is only complete after heating for from two and a-half to three hours. The hydroxy-anhydride remains as a gum on evaporating the reagent, and can be obtained crystalline by rubbing with dry ether. It separates from a mixture of benzene and light petroleum (b. p. 60—70°) in colourless, flat prisms, which melt at 69°:

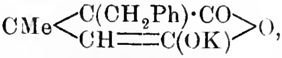
0·1997 gave 0·5295 CO_2 and 0·0970 H_2O. C=72·30; H=5·40.

$C_{13}H_{12}O_3$ requires C=72·2; H=5·5 per cent.

The compound gives no marked coloration with ferric chloride. It behaves on titration as a monobasic acid:

0·1753 required 4·25 c.c. NaOH solution (1 c.c.=0·00785 gram NaOH).

$C_{13}H_{12}O_3$ (monobasic) requires 4·15 c.c.

The *potassium* salt,  $CMe<\begin{matrix}C(CH_2Ph)\cdot CO\\ CH{=\!=}C(OK)\end{matrix}>O$, is precipitated as an oil, which crystallises on scratching, when excess of concentrated aqueous potassium hydroxide is added to a solution of the hydroxy-anhydride in dilute alkali:

0·2714 gave 0·0919 K_2SO_4. K = 15·18.

$C_{13}H_{11}O_3K$ requires K = 15·35 per cent.

The Hydration of the Hydroxy-anhydride: (a) *Water.*—When the hydroxy-anhydride is boiled with water, the normal acid melting at 148° is the sole product. (b) *Concentrated Alkali Hydroxide.*—Five grams of the hydroxy-anhydride were dissolved in sufficient dilute alkali to form a clear solution, and then mixed with a large excess of concentrated alkali. The precipitated alkali salt solidified on scratching, and a test portion was filtered and the filtrate acidified in order to show that the whole of the salt of the hydroxy-anhydride had been precipitated. The product was then kept at 30° for six hours, after which time the clear solution failed to deposit any unaltered salt, even on cooling to 0°; it was therefore concluded that the whole of the hydroxy-anhydride had been hydrated. The solution was then acidified with acetic acid and the crystalline precipitate isolated; it proved to be the hydroxy-anhydride melting at 69°, and the amount weighed 2·2 grams.

Sufficient hydrochloric acid to combine with the whole of the alkali originally used was then added to the filtrate, and the precipitated acid collected. It was found to be the acid melting at 134°, and was identified by direct comparison with this substance.

(c) *Dilute Alkali in the Presence of Casein.*—The conditions employed were as follows: 0·25 gram of the hydroxy-anhydride with 0·1 gram of casein was dissolved in excess (2 mols.) of *N*/10-sodium carbonate solution, and allowed to remain for four days at room temperature. The compound, isolated either through the silver salt or by acidifying with acetic acid, proved to be the hydroxy-anhydride melting at 69°. Since the solution before acidification was found to be practically neutral to litmus, it may be calculated that the whole of the hydroxy-anhydride had been hydrated.

The Aniline Derivatives of α-Benzyl-β-methylglutaconic Acid:

The Semianilide, $CO_2H{\cdot}C(CH_2Ph){:}CMe{\cdot}CH_2{\cdot}CO{\cdot}NHPh$.

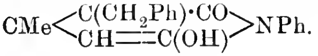
This substance is precipitated when a solution of the hydroxy-anhydride in benzene is mixed with aniline. It crystallises from dilute alcohol as lustrous plates, which melt at 149°:

0·1942 gave 0·5244 CO_2 and 0·1088 H_2O. C = 73·66; H = 6·23.

$C_{19}H_{19}O_3N$ requires C = 73·8; H = 6·1 per cent.

The semianilide is readily soluble in dry ether, and is converted into the hydroxy-anil when heated at 160°.

The Hydroxy-anil of α-Benzyl-β-methylglutaconic Acid (*3-Hydroxy-2-phenyl-6-benzyl-5-methyl-1 : 2-dihydropyridone*),



$$\mathrm{CMe}<\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}C(OH)}\end{matrix}>\mathrm{NPh}.$$

This substance is formed either by heating the semianilide at 160° for fifteen minutes or by heating 1·35 grams of either modification of the acid with 0·5 gram of aniline at 160° for the same length of time. It is isolated by rubbing the fused product with dry ether, in which it is insoluble, and can be obtained in flattened needles melting at 128° by recrystallisation from alcohol:

0·1268 gave 0·3650 CO_2 and 0·0670 H_2O. C = 78·48; H = 5·87.

$C_{19}H_{17}O_2N$ requires C = 78·3; H = 5·8 per cent.

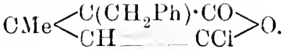
The compound dissolves in aqueous sodium carbonate, and behaves on titration as a monobasic acid:

0·2581 required 4·5 c.c. NaOH-solution (1 c.c. = 0·00785 gram NaOH).

$C_{19}H_{17}O_2N$ (monobasic) requires 4·52 c.c.

The colour of the indicator does not return on keeping, and the neutral solution is not altered on boiling.

The Chloro-anhydride (*6-Chloro-3-benzyl-4-methyl-α-pyrone*),



$$\mathrm{CMe}<\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}CCl}\end{matrix}>\mathrm{O}.$$

This substance is formed in small amount by the prolonged action of acetyl chloride on either modification of the acid at the temperature of the boiling reagent, but is produced in considerable quantity when the acid is heated with five times its weight of acetyl chloride in a sealed tube at 100° for three hours. It can be isolated from the product, freed from acetyl chloride, by dissolving it in ether and shaking with aqueous sodium hydrogen carbonate to remove acid constituents. The ether residue remained as a gum even after many months, and we have not as yet been able to crystallise this substance:

0·2317 gave 0·1396 AgCl. Cl = 14·92.

$C_{13}H_{11}O_2Cl$ requires Cl = 15·15 per cent.

The compound can be characterised by the formation of the *dianilide*, $NHPh\cdot CO\cdot C(CH_2Ph)\cdot CMe\cdot CH\cdot CO\cdot NHPh$, a substance which can be prepared by adding aniline to a benzene solution of the chlorine derivative, and can be isolated by shaking an ethereal solution of the product, freed from benzene, first with dilute hydrochloric acid, and then with aqueous sodium carbonate; the ethereal solution yields the dianilide on evaporation. It crystallises from alcohol containing a little water in silky needles, which melt at 190°:

0·1756 gave 0·5020 CO_2 and 0·0950 H_2O. C=77·96; H=6·01.
$C_{25}H_{24}O_2N_2$ requires C=78·1; H=6·2 per cent.

The dianilide is readily soluble in ether or benzene.

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THE UNIVERSITY SHEFFIELD.

CLXXXV.—*The Configuration of Substituted Ammonium Compounds.*

By HUMPHREY OWEN JONES and JOHN GUNNING MOORE DUNLOP.

OF the configurations suggested for the arrangement of groups around a quinquevalent nitrogen atom, the two which have met with most favour are the "double tetrahedron" configuration, suggested by Willgerodt, and the "pyramid" configuration, suggested by Bischoff.

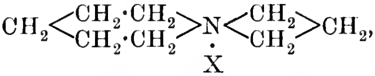
Both of these arrangements account for the existence of optically active compounds of the type NabcdX, but neither of them accounts for the non-existence of isomerides in which the alkyl groups occupy different relative positions in compounds of this type and in those of the type Na_2bcX. The absence of isomerism in these cases is accounted for, however, by a hypothesis as to the mode of union of tertiary amines and alkyl halides to form quaternary ammonium compounds having the pyramid configuration (see Jones, Trans., 1905, **87**, 1721).

On the "pyramid" or the "double tetrahedron" configuration for quinquevalent nitrogen compounds, it is to be expected that α- and β-substituted pyridinium and quinolinium compounds would exhibit optical activity, but despite the fact that many compounds of this type have been examined and described (see Jones, Trans., 1903, **83**, 1415; Buckney and Jones, Trans., 1907, **91**, 117), and a larger number of others have been studied by Miss M. B. Thomas, the results of whose work have not yet been published, no indication of optical activity has been found; the conclusion that compounds of this type cannot exhibit optical activity would therefore seem to be inevitable, and some explanation of this is desirable.

A new type of optically active compound, Nabc:O, has been discovered by Meisenheimer (*Ber.*, 1908, **48**, 3961; *Annalen*, 1911, **385**, 117), and several examples of this have been described.

The existence of enantiomorphism among compounds of this type is readily accounted for on the pyramid configuration, if it is assumed that one of the two valencies of the nitrogen atom which are satisfied by the oxygen atom is that one which is directed towards the apex of the pyramid, and to which the electronegative radicle is attached in ammonium salts.

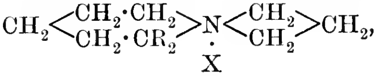
A consideration of the reasons for the absence of activity in pyridinium and quinolinium compounds led us to investigate the question of the existence of enantiomorphous forms of dicyclic quaternary ammonium compounds. The first example of this type of compound was described by Gabriel and Stelzner (*Ber.*, 1896, **29**, 2381).



$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\underset{\mathrm{X}}{\underset{\cdot}{\mathrm{N}}}{<}\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH_2},$$

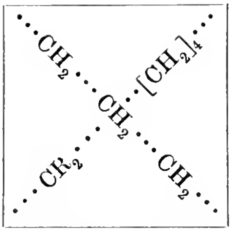
A consideration of a model of a compound of this type shows at once that, if the valencies of the nitrogen atom are arranged according to the "double tetrahedron" configuration, then the above should exist in enantiomorphous forms, whereas on the "pyramid" configuration this would not be the case.

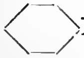
However, if one of the places of symmetry in one of the rings be destroyed, as, for example, in the compound



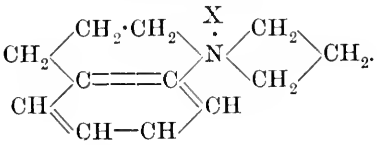
$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CR_2}\end{matrix}{>}\underset{\mathrm{X}}{\underset{\cdot}{\mathrm{N}}}{<}\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH_2},$$

there should be enantiomorphism, provided that the two rings do not interlace, thus:

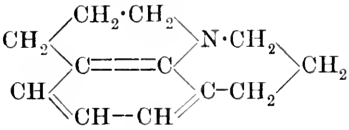


A consideration of the mode of formation of such a compound from $\mathrm{N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2X}$ shows that such an interlacing arrangement is improbable; therefore, a compound of this type would be expected to exhibit optical activity.

The simplest compound having the required structure would be a derivative of 2:2- or 3:3-dimethylpiperidine, but these compounds are not known, and, as the syntheses examined by one of us have given but poor yields, attention was turned to tetrahydroquinoline in the hope of obtaining the compound:

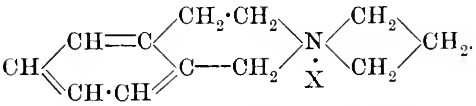


The required tertiary amine, γ-bromo- or -iodo-propyltetrahydroquinoline, was easily obtained, but on heating this gave a salt of another tertiary base, namely, julolidine:



(Pinkus, *Ber.*, 1892, **25**, 2802), instead of the expected quaternary compound.

Compounds of the desired type were, however, readily obtained from tetrahydro*iso*quinoline, namely, 2-*trimethylenetetrahydro*iso*quinolinium* salts, having the formula:



Several salts of this compound with optically active acids were prepared and examined, but no evidence of resolution into optical antimerides could be obtained.

It is easy to draw erroneous conclusions from negative evidence, but considering the above experiments, together with the well-established fact that α- and β-substituted pyridinium and also quinolinium compounds have not been obtained in optically active forms, it would seem that some explanation of the absence of optical activity in these cases must be sought in the arrangement of groups around the quinquevalent nitrogen atom.

On the view put forward by Werner ("Stereochemie," p. 310) ammonium salts are represented as (a_3·N . . . . b)X, but the assumption that one of the four alkyl groups is linked to the nitrogen atom in a manner which is distinguishable in any way from that in which the other alkyl groups are linked, leads to the conclusion that four isomerides of the type NabcdX should exist, each of which ought to be capable of resolution into two optical antimerides; this conclusion is clearly erroneous, as no isomerism other than optical isomerism has been shown to exist in compounds of this type.

A modification of this view would explain the known facts in a simple manner. If it be assumed that when a tertiary amine (Na_3) unites with an alkyl halide, aX, the four alkyl groups arrange themselves symmetrically around the nitrogen atom to form a group (Na_4) having enough residual valency to unite with an electronegative radicle, which is capable of acting as an ion.

This arrangement would be comparable to that which is assigned by Werner to the cobaltammines and similar compounds.

On this view of the structure of ammonium compounds it would naturally follow that the central group (Na_4) would have a configuration similar to methane, so that a group Nabcd would exhibit enantiomorphism. At present no hypothesis can be formulated as to the position or mode of linking of the electronegative radicle.

An apparent difficulty arises with regard to the representation of the amine-oxides $Na_3{:}O$, as it must be assumed that one of the valencies of the atom of oxygen satisfies one of the valencies of the nitrogen atom, which are supposed to be directed to the angular points of a tetrahedron, whilst the remaining oxygen valency satisfies the residual valency of the whole group. This is not a serious difficulty; and further, the salts all have the constitution $Na_3(OH)X$, in which the hydroxyl radicle functions as an alkyl group.

The view suggested above must be regarded for the present as tentative only, and more evidence is being accumulated to determine whether dicyclic compounds of the type described herein can exhibit optical activity or not; if further experiments show that compounds of this type as well as α- and β-substituted pyridinium compounds and quinolinium compounds do not exhibit optical activity, there would seem to be no alternative but to represent substituted ammonium compounds as constituted of a central group (Na_4) which possesses residual valency enabling it to form salts Na_4X.

EXPERIMENTAL.

The methods adopted for the preparation of the tetrahydroquinoline and tetrahydro*iso*quinoline bases of the type $C_9H_{10}N{\cdot}[CH_2]_3X$ were identical in almost all cases with those described by Gabriel and Stelzner (*loc. cit.*) for the preparation of the analogous piperidine base, $C_5H_{10}N{\cdot}[CH_2]_3X$, and it is therefore unnecessary to give details of the various processes, except in cases where deviations from these methods were required.

The preparation may be summarised as follows: The base,

$C_9H_{10}NH$, is heated with α-chloro-γ-phenoxypropane,

$PhO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl$,

to obtain the base $C_9H_{10}N{\cdot}[CH_2]_3{\cdot}OPh$. This is then heated to 100° with excess of fuming hydrobromic or hydriodic acid, giving the salt $C_9H_{10}N{\cdot}[CH_2]_3X,HX$, from which the base

$C_9H_{10}N{\cdot}[CH_2]_3X$

is obtained by the action of potassium hydroxide.

Tetrahydroquinoline Derivatives.

1-γ-*Phenoxypropyltetrahydroquinoline*, $C_9H_{10}N{\cdot}[CH_2]_3{\cdot}OPh$.—When α-chloro-γ-phenoxypropane is heated with tetrahydroquinoline it is found that the solid product of the reaction is tetrahydroquinoline hydrochloride, and for this reason it is necessary to use two molecules of base to one of the chloro-ether. This greatly increased the yield, and was adopted in all such reactions.

An additional advantage of the use of excess of base is that the whole of the chloro-ether is used up, which renders the precautions which were taken by Gabriel to ensure its removal unnecessary, and after twenty-four hours' heating on the water-bath the reaction mixture can be treated directly with potassium hydroxide, and the bases removed and fractionated.

1-γ-*Phenoxypropyltetrahydroquinoline* is a clear, pale yellow, viscid oil, which boils at 256°/20 mm.:

0·2047 gave 0 6055 CO_2 and 0·1404 H_2O. C = 80·6; H = 7·63.

$C_{18}H_{21}ON$ requires C = 80·9; H = 7·87 per cent.

All attempts to prepare a crystalline derivative of the base were unsuccessful.

1-γ-*Bromopropyltetrahydroquinoline hydrobromide*,

$C_9H_{10}N{\cdot}[CH_2]_3Br,HBr$,

separates from alcohol in colourless prisms which melt at 195°:

0·2283 gave 0·3600 CO_2 and 0·1020 H_2O. C = 43·0; H = 4·9.

0·2563 „ 0·2888 AgBr. Br = 47·8.

$C_{12}H_{17}NBr_2$ requires C = 43·0; H = 5·07; Br = 47·8 per cent.

1-γ-*Iodopropyltetrahydroquinoline hydriodide*,

$C_9H_{10}N{\cdot}[CH_2]_3I,HI$,

crystallises from alcohol in colourless prisms melting at 167°:

0·2308 gave 0·2850 CO_2 and 0·0825 H_2O. C = 33·7; H = 3·97.

$C_{12}H_{17}NI_2$ requires C = 33·6; H = 3·96 per cent.

During the heating of the phenoxypropyl base with fuming hydriodic acid, some dark green, needle-shaped crystals were also formed; these are decolorised by sulphurous acid, giving the normal product of the reaction. They appeared to be a periodide, but were not further examined.

The bases, $C_9H_{10}N{\cdot}[CH_2]_3X$, obtained from these salts when heated on the water-bath are converted into crystalline salts in periods varying from fifteen minutes for the iodo- to sixteen hours in the case of the bromo-base. These salts proved to be the hydriodide and hydrobromide respectively of julolidine (Pinkus, *loc. cit.*), melting at 223° and 227° respectively.

*Tetrahydro*iso*quinoline Derivatives.*

2-γ-*Phenoxypropyltetrahydro*iso*quinoline*, $C_9H_{10}N\cdot[CH_2]_3\cdot OPh$, is an alkaline oil which boils at 265°/10 mm. With hydrochloric acid it gives a *hydrochloride*, crystallising in plates which melt at 193°:

0·2537 gave 0·6595 CO_2 and 0·1650 H_2O. C=70·9; H=7·23.
$C_{18}H_{22}ONCl$ requires C=71·2; H=7·25 per cent.

2-γ-*Iodopropyltetrahydro*iso*quinoline hydriodide*,

$$C_9H_{10}N\cdot[CH_2]_3I,HI,$$

separates from alcohol in colourless prisms melting at 145°:

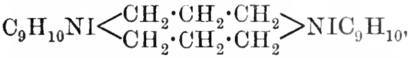
0·3455 gave 0·4225 CO_2 and 0·1225 H_2O. C=33·42; H=3·94.
$C_{12}H_{17}NI_2$ requires C=33·6; H=3·96 per cent.

The base obtained from this salt by the action of potassium hydroxide is very rapidly converted when heated on the water-bath into a crystalline salt, which is very sparingly soluble in all solvents except methyl alcohol, from which it separates in colourless needles melting at 169°. The salt resolidifies a little above its melting point, and melts again with decomposition at 235°:

0·2735 gave 0·4755 CO_2 and 0·1320 H_2O. C=47·4; H=5·3.
$C_{12}H_{16}NI$ requires C=47·8; H=5·3 per cent.

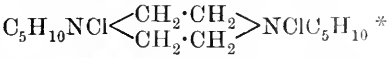
The *platinichloride* crystallises in yellow needles melting at 183°. This salt, therefore, is clearly 2-*trimethylenetetrahydro*iso*quinolinium iodide*, a dicyclic quaternary ammonium compound of the desired type.

In addition to these crystals a certain proportion of a white, amorphous salt, which is insoluble in all solvents, is always obtained. A satisfactory analysis of this could not be made, as it contained a variable proportion of inorganic matter. The melting point is above 300°. It is surmised that it is a condensation product of two molecules of the iodo-base of the formula:



$$C_9H_{10}NI<\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\CH_2\cdot CH_2\cdot CH_2\end{matrix}>NIC_9H_{10},$$

as an analogous compound is obtained on heating 1-β-chloroethylpiperidine, $C_5H_{10}N\cdot CH_2\cdot CH_2Cl$, the formula in this case being



$$C_5H_{10}NCl<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NClC_5H_{10}\ *$$

(compare also Hörlein and Kniesel, *Ber.*, 1906, **39**, 1429).

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* A paper on this subject will shortly be communicated by one of us.

*Attempts to Resolve 2-Trimethylenetetrahydro*iso*quinolinium Salts.*

The salts of 2-trimethylenetetrahydro*iso*quinolinium with various optically active acids were made, with the exception of the tartrate, by boiling a mixture in equivalent proportions of the iodide described above, and the silver salt with a mixture of ethyl acetate, alcohol, and water, filtering from silver iodide, and evaporating the filtrate (Pope and Peachey's method). The crystalline salt so obtained was recrystallised several times from a suitable solvent, and the rotatory power determined in aqueous solution in a 2-dcm. tube.

The d-*α-camphorsulphonate* crystallises from acetone in plates melting at 142°. After being three times recrystallised, 0·3566 in 12·34 of solution gave α_D 0·72°, whence $[\alpha]_D$ 12·4°, $[M]_D$ 50·4°. $[M]_D$ for acid ion = 51·7°. Hence there is no resolution.

The d-*β-camphorsulphonate* crystallises from acetone in needles melting at 186°. After being recrystallised three times, 0·2341 in 13·4 of solution gave α_D 1·49°, whence $[\alpha]_D$ 45·1°, $[M]_D$ 175°. $[M]_D$ for acid ion = 170°. Hence there is no resolution.

The d-*α-bromo-β-camphorsulphonate* separates from a mixture of acetone and benzene in needles melting at 175°. After being three times recrystallised, 0·213 in 12·35 of solution gave α_D 1·93°, whence $[\alpha]_D$ 55·9°, $[M]_D$ 271°. $[M]_D$ for acid ion = 277°. Hence there is no resolution.

The d-*α-chloro-β-camphorsulphonate* crystallises from acetone in plates melting at 177°. After being many times recrystallised, 0·1672 in 12·36 of solution gave α_D 1·145°, whence $[\alpha]_D$ 43·2°, $[M]_D$ 190°. $[M]_D$ for acid ion = 185°. Hence there is no resolution.

The d-*tartrate* was prepared by half neutralising the hydroxide with tartaric acid. The mixture never yielded any crystals which could be separated.

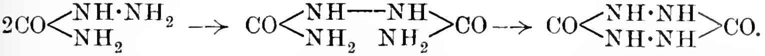
The expenses of this work were partly defrayed by grants from the Government Grant Committee of the Royal Society, for which we are glad to express our thanks.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CLXXXVI.—*The Action of Sodium Hypobromite on Carbamide Derivatives. Part I.*

By Frank William Linch.

p-Urazine may be obtained by the action of sodium hypobromite on semicarbazide. The maximum yield (80 per cent. of the theoretical) is obtained when the two compounds are used in the proportion of 2 molecules of semicarbazide to 3 molecules of sodium hypobromite. The reaction probably takes place in stages with the intermediate formation of hydrazodicarbonamide, and the fact that this substance is oxidised by sodium hypobromite to *p*-urazine supports this assumption:



$$2CO{<}\begin{matrix}NH\cdot NH_2\\NH_2\end{matrix} \longrightarrow CO{<}\begin{matrix}NH\text{——}NH\\NH_2\quad NH_2\end{matrix}{>}CO \longrightarrow CO{<}\begin{matrix}NH\cdot NH\\NH\cdot NH\end{matrix}{>}CO.$$

As Curtius has shown, *p*-urazine is very sensitive to oxidising agents, for example, in contact with a slight excess of hypobromite it changes to an orange, crystalline powder, which, as the ring structure remains intact, may have one of two formulæ:

$$CO{<}\begin{matrix}N{=\!=}N\\NH\cdot NH\end{matrix}{>}CO$$

(I.)

$$CO{<}\begin{matrix}N{:}N\\N{:}N\end{matrix}{>}CO$$

(II.)

Analysis indicates the former, and therefore the oxidation product is 3:6-*diketo*-1:2:3:6-*tetrahydro*-1:2:4:5-*tetrazine*. Attempts to prepare the bisazo-ring compound (II) were unsuccessful, as further oxidation completely decomposes the substance.

The azo-linking greatly decreases the stability of the ring for boiling dilute hydrochloric acid, hydrolyses the substance into carbon dioxide, nitrogen, and hydrazine hydrochloride, whereas *p*-urazine requires to be heated to 150° with concentrated hydrochloric acid before it undergoes a similar change.

Thiosemicarbazide and hydrazodicarbonthiamide when acted on by sodium hypobromite yield *hydrazodicarbonthiamidemonosulphonic acid*, $SO_3H\cdot C(:NH)\cdot NH\cdot NH\cdot C(:NH)\cdot SH$, which is formed from hydrazodicarbonthiamide by the addition of three atoms of oxygen.

Barnett (Trans., 1910, **97**, 63) has shown that a similar oxidation of a thiol group occurs during the oxidation of thiocarbamide to aminoiminomethanesulphinic acid, $NH_2\cdot C(:NH)\cdot SO_2H$. No condensation product can be obtained from carbamide itself, owing to its symmetrical nature, but by making the molecule unsymmetrical, for example, by acetylating one amido-group, condensation takes place across the unsubstituted amido-groups; thus, acetylcarbamide yields *diacetohydrazodicarbonamide*:

$$2NH_2\cdot CO\cdot NHAc \longrightarrow NHAc\cdot CO\cdot NH\cdot NH\cdot CO\cdot NHAc.$$

EXPERIMENTAL.

Action of Sodium Hypobromite on Semicarbazide.

Ten grams of semicarbazide hydrochloride were dissolved in 50 c.c. of water, and a solution of sodium hypobromite, containing 14·2 grams of sodium hydroxide in 100 c.c. of water and 7·1 c.c. of bromine, was added little at a time, the solutions being cooled. The excess of sodium hydroxide was used to liberate the semicarbazide from its hydrochloride.

There was a brisk evolution of nitrogen, and *p*-urazine was deposited as a fine, white, crystalline powder. After an hour it was collected and recrystallised from boiling water, from which it separated in small, brilliant crystals melting at 266°. The yield was 4 grams, or 80 per cent. of the theoretical. (Found, $N=48{\cdot}38$. $C_2H_4O_2N_4$ requires $N=48{\cdot}28$ per cent.)

In order to confirm the constitution, a small quantity was heated with concentrated sulphuric acid to 120—130°, and the resulting hydrazine sulphate was analysed. (Found, $H_2SO_4=75{\cdot}38$. Calc., $H_2SO_4=75{\cdot}37$ per cent.)

Action of Sodium Hypobromite on Hydrazodicarbonamide.

Owing to the sparing solubility of the substance in cold water, the reaction had to be carried out in very dilute solution, and a small quantity of acid was added to increase its solubility.

One gram of hydrazodicarbonamide was dissolved in 250 c.c. of water, and 10 c.c. of 3*N*-hydrochloric acid were added. The solution was allowed to cool to 35°, and one equivalent of hypobromite solution, containing sufficient sodium hydroxide to neutralise the added hydrochloric acid, was mixed with the hydrazodicarbonamide. A white, crystalline precipitate was gradually deposited, a much larger amount being obtained on evaporation. After recrystallisation from hot water, the substance melted at 266°, and was therefore *p*-urazine.

Oxidation of p-*Urazine to* 3:6-*Dikcto*-1:2:3:6-*tetrahydro*-1:2:4:5-*tetrazine.*

One and a-half grams of *p*-urazine were dissolved in boiling water, and a solution of 2 grams of potassium dichromate and 1 c.c. of concentrated sulphuric acid was added to the boiling solution, but prolonged boiling is inadvisable owing to the ease with which the oxidation product undergoes decomposition. On cooling, an orange, crystalline powder was deposited, which was best recrystallised from hot water. The substance separates in small, orange needles, which have no definite melting point, for at 216° there is decomposition with gas evolution and a simultaneous colour change from orange to white. The white product melts at 240°. The yield is 40 per cent. of the theoretical.

On reducing an aqueous solution with stannous chloride, a colourless solution is obtained, which deposits *p*-urazine on cooling, so that the ring structure is not destroyed during oxidation:

0·0577 gave 23·9 c.c. N_2 (moist) at 16° and 770 mm. N=49·3.
$C_2H_2O_2N_4$ requires N=49·12 per cent.

3:6-*Diketo*-1:2:3:6-*tetrahydro*-1:2:4:5-*tetrazine* is fairly soluble in boiling water, but practically insoluble in common organic solvents. It is readily hydrolysed by dilute acids to hydrazine salts, and does not condense with aldehydes or ketones, which is a characteristic of *p*-urazine.

Action of Sodium Hypobromite on Thiosemicarbazide.

Five grams of thiosemicarbazide were dissolved in 100 c.c. of water, and the required amount of dilute sodium hypobromite solution was added in small quantities, the mixture being kept below 30°. There was a brisk evolution of nitrogen, and the solution became strongly acid. The mixture was warmed to 40—50° until all the hypobromite had reacted, and was then evaporated considerably. The concentrated solution was cooled in ice, when, after some time, long, colourless needles crystallised out. During the concentration of the solution, a yellow colour is sometimes developed, due to the oxidation of the product, but a few drops of stannous chloride soon reduce it to the original substance.

After recrystallisation from dilute alcohol the needles melted and decomposed at 247°, evolving hydrogen sulphide and sulphur dioxide, and leaving a residue which had the appearance and properties of the ash left on burning mercuric thiocyanate. The crystals lose their lustre on drying at 100°, owing to loss of water of crystallisation.

Analysis of substance dried at 100°:

0·1609 gave 0·0722 CO_2 and 0·0414 H_2O. C=12·23; H=2·92.
0·1002 ,, 24·4 c.c. N_2 (moist) at 14° and 754 mm. N=28·64.
0·1503 ,, 0·3480 $BaSO_4$. S=31·72.

0·2056, dried in a vacuum, lost 0·0176 at 100°. $H_2O = 8·56$.
$C_2H_6O_3N_4S_2$ requires $C = 12·12$; $H = 3·03$; $N = 28·28$; $S = 32·3$ per cent.
$C_2H_6O_3N_4S_2,H_2O$ requires $H_2O = 8·33$ per cent.

Hydrazodicarbonthiamidemonosulphonic acid crystallises from water or alcohol in long, colourless needles. It decomposes sodium carbonate, and forms a dibasic *silver* salt, which leaves a residue of silver sulphide on ignition.

Action of Sodium Hypobromite on Acetylcarbamide: Preparation of Diacetohydrazodicarbonamide.

Two grams of acetylcarbamide were dissolved in 150 c.c. of water, and one-half an equivalent of sodium hypobromite was added to the well-cooled solution. The mixture was allowed to remain, and then evaporated considerably; on cooling, a white, crystalline precipitate was deposited. After recrystallisation from hot water, the product was obtained in fine, white crystals, melting above 300°. In another experiment the product consisted of a mixture of the above substance, and hydrazodicarbonamide (m. p. 245°) formed through hydrolysis during evaporation. The substance melting above 300° was dried at 100° and analysed:

0·0604 gave 13·8 c.c. N_2 (moist) at 10° and 760 mm. $N = 27·51$.
$C_6H_{10}O_4N_4$ requires $N = 27·72$ per cent.

In order to confirm the identity of the substance, hydrazodicarbonamide was acetylated, and the product was found to be identical with the above.

It is proposed to extend this research to other carbamide derivatives.

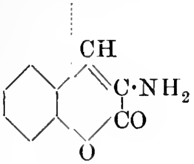
In conclusion, I wish to express my thanks to Dr. A. E. Dunstan, in whose laboratory the research was carried out, for the interest he has taken in this work.

East Ham Technical College.

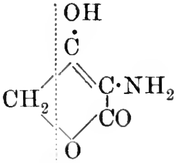
CLXXXVII.—3-*Aminocoumarin.*

By Frank William Linch.

All the aminocoumarins which have been investigated contain an amino-group attached to the benzene nucleus. It appeared therefore of interest to prepare one containing the amino-group in the closed aliphatic side-chain, and to ascertain to what extent the properties of the group are influenced by the presence of the attached aromatic nucleus. The structure of 3-aminocoumarin is very similar to that of aminotetronic acid (Wolff and Lüttringhaus, *Annalen*, 1900, **312**, 133):



3-Aminocoumarin.

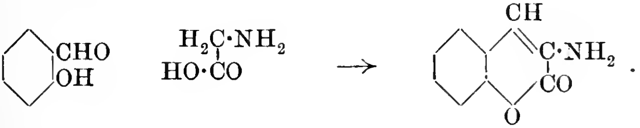


Aminotetronic acid.

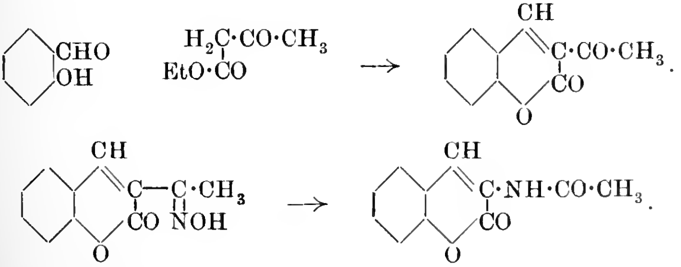
which is one of the few non-benzenoid cyclic systems known to furnish diazonium salts, and in the case of 3-aminocoumarin one would expect the attached benzene nucleus to enhance the aromatic nature of the amino-group.

On reviewing the possible ways of preparing the base, two methods suggested themselves:

(1) Condensation of salicylaldehyde and glycine by means of Perkin's reaction, but the yield of 3-acetylaminocoumarin was unsatisfactory, the maximum yield obtained being 25—30 per cent. of the theoretical:



(2) This method was more advantageous. The starting point was 3-acetylcoumarin, prepared by condensing salicylaldehyde and ethyl acetoacetate (Knoevenagel, *Ber.*, 1898, **31**, 732). The oxime of this substance was treated with phosphorus chlorides, when it underwent the Beckmann transformation, giving 3-acetylaminocoumarin:



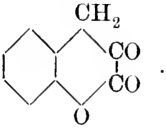
The base was obtained by careful hydrolysis.

The identity of the substance was confirmed by benzoylating it, and the 3-benzoylaminocoumarin obtained was identical with that obtained by Erlenmeyer, jun., and Stadlin (*Annalen*, 1904, **337**, 283) by the condensation of hippuric acid and salicylaldehyde.

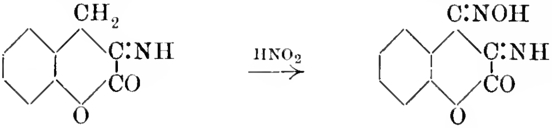
In its reactions, 3-aminocoumarin behaves as though it possesses the imino-structure, owing to the tendency of the side-chain to become saturated.

Nitrous acid gives a cream, semicrystalline substance from faintly acid solutions, which does not show Liebermann's reaction, nor does it respond to the tests for a diazo-oxide. Some difficulty was experienced in purifying this product, but the analytical results are in approximate agreement with the figures required on the assumption that the substance is an *iso*nitroso-compound.

Experiments tend to confirm this assumption; for example, (*a*) it possesses an acidic nature; (*b*) it gives a deep blue colour with ferrous sulphate when dissolved in the minimum amount of alkali, a characteristic of *iso*nitroso-compounds of similar structure; (*c*) on hydrolysis, 3-ketocoumarin is formed, which, as it readily forms an oxime, must possess the structure:

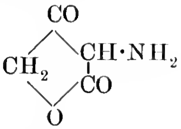


These experiments indicate an imino-structure for the base, and the action of nitrous acid can be represented as follows:



The base forms a *benzylidene* compound, but does not condense with nitrosobenzene, so probably in the formation of the first compound the aldehydic oxygen condenses with the hydrogen of the methylene group.

Coumarin readily combines with two atoms of bromine, causing the side-chain to become saturated, but 3-acetylcoumarin shows no tendency to absorb bromine, as would be expected, provided that it has the imino-structure, as the carbon atoms of the side-chain then become singly linked.

Boiling potassium or sodium hydroxide liberates ammonia from the base with the formation of 3-ketocoumarin, but sodium ethoxide and concentrated ammonia decompose the side-chain, forming salicylaldehyde and glycollic acid. Forster (Trans., 1909, **96**, 2074) suggests that the structure of aminotetronic acid is best represented by the formula , in which the carbon atoms become singly linked, and so Wolff's diazo-compound is brought into line with aliphatic diazo-compounds. In the case of 3-aminocoumarin the carbon atoms of the side-chain tend to become singly linked, and so it adds to the likelihood of Forster's being the correct explanation of the action of nitrous acid on aminotetronic acid.

The *iso*nitroso-compound being difficult to purify, the corresponding compound from 7-bromo-3-aminocoumarin was prepared, as the increase in molecular weight was expected to increase the crystallising powers of the substance, but a new difficulty was introduced, as owing to the feebly basic nature of the bromoaminocoumarin, it could only be retained in solution by the addition of a large excess of mineral acids, which prevented the formation of the *iso*nitroso-compound in any quantity.

EXPERIMENTAL.

3-*Acetylaminocoumarin.*

This substance was prepared from the oxime of acetylcoumarin by means of the Beckmann reaction. The oxime is remarkably stable towards concentrated sulphuric acid, and it is scarcely affected until near the boiling point of the acid, when it undergoes rapid decomposition. The most satisfactory manner of carrying out the transformation is as follows:

The dry oxime (5 grams) is carefully dissolved in phosphorus trichloride (25 c.c.) in a Wurtz flask. The solution is cooled, and about 2 grams of powdered phosphorus pentachloride are added, the mixture being cooled if necessary, for sometimes there is considerable heat evolution. The phosphorus trichloride is then distilled off under diminished pressure, and the contents of the flask poured on to powdered ice. 3-Acetylaminocoumarin is deposited as a pale yellow, amorphous powder, and it is advisable to collect it at once. If allowed to remain in contact with the acid liquid, the substance turns green, and it is somewhat difficult to remove the colour during the purification of the acetyl compound.

The impure substance is easily purified by dissolving it in aqueous alcohol and boiling with animal charcoal. On filtering and allowing the solution to remain, 3-acetylaminocoumarin separates in long, silky needles.

It crystallises from alcohol, acetone, and most organic solvents in long, colourless needles, melting at 201·5°. The yield is 75 per cent. of the theoretical:

0·3968 gave 24·2 c.c. N_2 (moist) at 22° and 751 mm. N=6·86.

$C_{11}H_9O_3N$ requires N=6·89 per cent.

3-*Aminocoumarin*.

The acetyl derivative just described is dissolved in hydrochloric acid (1:2), and the solution boiled for ten minutes. A crystalline precipitate of the hydrochloride of the base is gradually deposited. The acid solution is then neutralised with sodium carbonate, when the base is deposited as a cream-coloured, semi-crystalline powder. On recrystallisation from dilute alcohol, animal charcoal being present, it separates in small, cream-coloured needles, melting at 130°. The yield is 65 per cent. of the theoretical.

Care has to be exercised during the hydrolysis of the acetyl group, for prolonged boiling eliminates the amino-group, with the formation of 3-ketocoumarin. There is always a little of this substance produced, but its separation offers no difficulties owing to its solubility being much less than that of the base.

3-*Aminocoumarin* is sparingly soluble in cold, but readily so in hot, water, and separates from this solvent in flat needles. It also crystallises well from most organic solvents:

0·1689 gave 0·4136 CO_2 and 0·0648 H_2O. C=66·79; H=4·27.
0·1532 „ 11·8 c.c. N_2 (moist) at 20° and 745 mm. N=8·69.

$C_9H_7O_2N$ requires C=67·08; H=4·35; N=8·69 per cent.

The Hydrochloride.—The base is dissolved in absolute alcohol, and dry hydrogen chloride passed into the solution. The precipitated hydrochloride is collected, washed with absolute alcohol, and dried under diminished pressure.

It forms white, pearly plates, which are considerably hydrolysed when dissolved in water:

0·1586 gave 0·1168 AgCl. HCl=18·75.

$C_9H_7O_2N,HCl$ requires HCl=18·48 per cent.

The *platinichloride* is a heavy, yellow precipitate:

0·2817 gave 0·0746 Pt. Pt=26·48.

$(C_9H_7O_2N,HCl)_2PtCl_4$ requires Pt=26·63 per cent.

The *sulphate* is obtained in white, pearly plates when a few drops of concentrated sulphuric acid are added to a solution of the base in absolute alcohol. It is largely hydrolysed when dissolved in water.

3-*Benzylideneaminocoumarin.*

Approximately equal weights of benzaldehyde and 3-aminocoumarin are gently warmed until a colourless solution is obtained. On cooling, this solidifies to a white cake, which is boiled several times with alcohol to remove any unchanged benzaldehyde or base. The compound is sparingly soluble in organic solvents, and is most conveniently crystallised from chloroform. It forms a white, crystalline powder, melting at 160°, which is readily decomposed into its constituents by dilute acids:

0·1521 gave 7·1 c.c. N_2 at 8° and 768 mm. N=5·69.
$C_{16}H_{11}O_2N$ requires N=5·62 per cent.

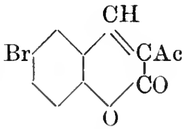
Action of Nitrous Acid on 3-Aminocoumarin.

Two grams of the base were dissolved in 250 c.c. of water, to which three equivalents of hydrochloric acid had been added. The solution was cooled in ice, and the requisite amount of sodium nitrite solution (1:10) run in. There was no evolution of nitrogen, but a cream-coloured, semi-crystalline solid was precipitated. The amount of this product obtained depends on the concentration of the acid solution, for as the proportion of the latter increases, so a proportionately smaller amount of the former is obtained.

The precipitated solid (1·3 grams) was collected, well washed, and dried under diminished pressure. Difficulty was experienced in crystallising the substance, and the most convenient method was to dissolve it in acetone, add alcohol, and allow the solution to remain. The product is deposited as a pale, straw-coloured, crystalline powder, melting and decomposing at 232°. It is decomposed by boiling with dilute acids, in which it gradually dissolves. It is readily soluble in alkalis, and, as mentioned above, reacts as an *iso*nitroso-compound:

0·1234 gave 0·2568 CO_2 and 0·0401 H_2O. C=56·75; H=3·61.
0·082 „ 10·3 c.c. N_2 (moist) at 20° and 760 mm. N=14·50.
$C_9H_6O_3N_2$ requires C=56·84; H=3·15; N=14·73 per cent.

7-Bromo-3-acetylcoumarin,



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Twenty-five grams of 5-bromosalicylaldehyde were dissolved in 18 grams of ethyl acetoacetate with the assistance of a little absolute alcohol. The hot solution was allowed to cool to about 40°, so that no crystals were deposited, and then 2 grams of piperidine were added. The liquid became semi-solid, and, on cooling, solidified to a yellow, crystalline cake. This was ground up with a little alcohol, collected, and washed. The residue was crystallised from boiling alcohol, in which it is not very soluble. After some time cream-coloured needles separated, which retained their colour after repeated boiling with animal charcoal.

7-Bromo-3-acetylcoumarin crystallises from glacial acetic acid or benzene in flat needles of a primrose colour. It is sparingly soluble in acetone, chloroform, or light petroleum, and melts at 217°:

0·1570 gave 0·1110 AgBr. Br = 30·05.

$C_{11}H_7O_3Br$ requires Br = 29·96 per cent.

The oxime could not be obtained by any of the usual methods owing to the sparing solubility of bromoacetylcoumarin. The following method was adopted: Equivalent quantities of the two substances, that is, 14·1 grams of 7-bromo-3-acetylcoumarin and 3·48 grams of hydroxylamine hydrochloride, were dissolved separately in the smallest possible quantities of boiling glacial acetic acid. The solutions were allowed to cool until signs of crystallisation appeared, and then they were mixed. On keeping, the *oxime* was deposited in pale yellow, crystalline crusts.

It is almost insoluble in benzene, alcohol, etc., and was recrystallised from hot glacial acetic acid. The oxime decomposes before melting, darkening from 190°, and at 220° passes into a brownish-black liquid with gas evolution:

0·2304 gave 0·1553 AgBr. Br = 28·64.

$C_{11}H_8O_3NBr$ requires Br = 28·36 per cent.

7-Bromo-3-acetylaminocoumarin.

When the oxime of 7-bromo-3-acetylcoumarin is treated with phosphorus chlorides by the method previously described, it undergoes the Beckmann transformation with the formation of the above substance. This crystallises from alcohol, glacial acetic acid, and most common organic solvents in long needles, melting at 266°.

Any unchanged oxime is best removed by fractional crystallisation from benzene, the oxime being the less soluble:

0·3010 gave 0·2009 AgBr. Br = 28·40.

$C_{11}H_8O_3NBr$ requires Br = 28·36 per cent.

7-Bromo-3-aminocoumarin.

In this case it was found more convenient to use sulphuric acid as the hydrolysing agent, owing to the greater solubility of the acetyl compound in this acid. The acetyl compound was suspended in water, and then concentrated sulphuric acid was added until the substance passed into solution. The solution was boiled gently for ten minutes, and after cooling and diluting, practically the whole of the bromo-base was precipitated owing to its feebly basic properties. This was collected, and the small amount of colouring matter present was removed by boiling the alcoholic solution with animal charcoal. The base crystallises from alcohol, chloroform, or acetone in pale cream needles, and from benzene in plates. It melts at 205°:

0·1108 gave 0·0866 AgBr. Br = 33·22.

$C_9H_6O_2NBr$ requires Br = 33·33 per cent.

Condensation of Salicylaldehyde with Glycine.

Many experiments were carried out under varying conditions, but the maximum yield of 3-acetylaminocoumarin obtained was 25—30 per cent. of the theoretical.

The most satisfactory method of bringing about the condensation was as follows: Five grams of glycine, 8 grams of salicylaldehyde, 7·5 grams of fused sodium acetate, and 20 grams of acetic anhydride were mixed together and heated in an oil-bath at 120° for six hours. The mixture soon melted to a yellow liquid, which darkened considerably during the heating.

On cooling, the contents of the flask solidified to a semi-crystalline cake, which was crystallised from a mixture of alcohol and water. The 3-acetylaminocoumarin was obtained as a yellow, crystalline powder, which after two crystallisations from boiling water separated in long, white needles, melting at 201°. (Found, N = 6·97. Calc., N = 6·89 per cent.)

The author wishes to express his gratitude to Dr. W. H. Mills for the valuable advice given during the course of this investigation.

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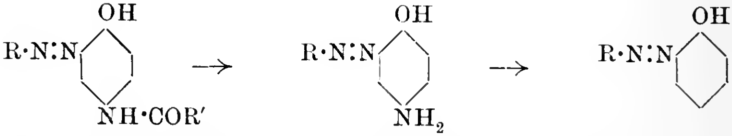
CLXXXVIII.—*Derivatives of* o-*Hydroxyazobenzene.*

By John Theodore Hewitt and William Henry Ratcliffe.

In the course of some work at present in progress, the authors of this communication found it desirable to work out a method whereby *o*-hydroxyazobenzene and compounds derived from it might be obtained with relative ease. Bamberger has demonstrated the presence of *o*-hydroxyazobenzene amongst the products of isomerisation of azoxybenzene (*Ber.*, 1900, **33**, 1933); it is also formed to the extent of about 1 per cent. when benzenediazonium salts react with an alkaline solution of phenol (*Ber.*, 1900, **33**, 3188), the para-isomeride forming by far the chief product of the reaction.

It seemed probable that a convenient source of the *o*-hydroxyazo-compound and its derivatives might be found in *p*-acetylaminophenol (or other acyl derivative), which might be coupled with diazonium salts, and the acyl- and amino-groups subsequently eliminated:



The reactions followed the expected course, but during the progress of the work a paper appeared by N. N. Voroschtsoff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 787), in which the preparation of *m*-acetylamino-*o*-hydroxyazobenzene and *o*-hydroxyazobenzene was described. The *m*-amino-*o*-hydroxyazobenzene obtained as an intermediate compound was also isolated, but no other derivatives were made. As we already possess a considerable number of compounds obtained by coupling the diazonium salts derived from substituted anilines with *p*-acetylaminophenol, whilst our method differed in that we used sodium acetate instead of sodium carbonate to neutralise the acid during the coupling process, the results so far obtained will be described. In alkali hydroxide solutions much frothing took place, and the yield of acetylaminohydroxyazobenzene was poor; much better results were obtained when sodium acetate was used, and Voroschtsoff states that he obtained 17·5 grams of crystallised product, starting with 12 grams of acetylaminophenol and 7·5 grams of aniline.

EXPERIMENTAL.

The requisite *p*-acetylaminophenol was prepared by boiling equal weights of *p*-aminophenol and glacial acetic acid under reflux for six hours and purified by crystallisation from hot water. It melts at 166—167° (uncorr.) (166°, Friedländer, *Ber.*, 1893, **26**, 178; 165°, Voroschtsoff, *loc. cit.*).

m-*Acetylamino*-o-*hydroxyazobenzene*.—A solution made by diazotising 9·3 grams of aniline dissolved in 28·5 c.c. of fuming hydrochloric acid and 120 c.c. of water with 6·9 grams of sodium nitrite in 20 c.c. of water was added to a solution of 15·1 grams of *p*-acetylaminophenol in 400 c.c. of alcohol, to which 40 grams of sodium acetate were added. The product of coupling separates as a yellow precipitate; after crystallising from alcohol it formed needles melting at 226°, in agreement with Voroschtsoff's statement. (Found, C = 65·7; H = 5·1; N = 16·8. $C_{14}H_{13}O_2N_3$ requires C = 65·9; H = 5·1; N = 16·5 per cent.)

m-*Amino*-o-*hydroxyazobenzene*.—Voroschtsoff has isolated and analysed the free base; the preparation of salts is, however, sufficient to demonstrate the removal of the acetyl group.

The Hydrochloride.—This brown salt was obtained by heating 2 parts of the acetylamino-compound, 3 parts of hydrochloric acid, and 15 parts of alcohol on the water-bath for two hours, evaporating to dryness, and recrystallising from hot dilute hydrochloric acid. The salt decomposes at about 205°; it gives a deep red solution in alkalis:

0·2031 gave 0·4277 CO_2 and 0·0908 H_2O. C = 57·4; H = 5·0.
0·2572 „ 36·8 c.c. N_2 at 20° and 770 mm. N = 16·7.
0·3125 „ 0·1802 AgCl. Cl = 14·25.
$C_{12}H_{12}ON_3Cl$ requires C = 57·6; H = 4·8; N = 16·8;
Cl = 14·2 per cent.

The Hydrogen Sulphate.—By treating the hydrochloride with an excess of concentrated sulphuric acid in the cold, and crystallising the product from hot water, dark red needles are obtained, which decompose at a high temperature. Analysis showed that the substance was the hydrogen sulphate:

0·2169 gave 25·8 c.c. N_2 at 20° and 756 mm. N = 13·7.
0·6256 „ 0·4729 $BaSO_4$. H_2SO_4 = 31·7.
$C_{12}H_{11}ON_3,H_2SO_4$ requires N = 13·5; H_2SO_4 = 31·5 per cent.

If the sulphate is boiled with alcohol and the calculated amount of sodium nitrite, *o*-hydroxyazobenzene melting at 82° may be obtained by steam distillation and crystallisation from ether. The yield is about 50 per cent. of that required by theory.

m-*Acetylamino*-o-*acetoxyazobenzene*,

$$C_6H_5\cdot N{:}N\cdot C_6H_3(NH\cdot CO\cdot CH_3)\cdot O\cdot CO\cdot CH_3,$$

is obtained by suspending acetylaminohydroxyazobenzene in three times its weight of acetic anhydride, adding one or two drops of concentrated sulphuric acid, boiling for forty minutes, and pouring into water. After addition of sodium hydroxide, collection, and crystallisation from glacial acetic acid, orange-yellow crystals are obtained, melting at 196—198°:

0·1909 gave 0·4522 CO_2 and 0·0852 H_2O. C = 64·6; H = 4·95.
0·1956 „ 23·8 c.c. N_2 at 17·5° and 760 mm. N = 14·1.
$C_{16}H_{15}O_3N_3$ requires C = 64·6; H = 5·05; N = 14·1 per cent.

A triacetyl derivative would require C=63·7; H=5·0; N=12·4 per cent.

o′-*Chloro*-m-*acetylamino*-o-*hydroxyazobenzene*,

$C_6H_4Cl\cdot N:N\cdot C_6H_3(OH)\cdot NH\cdot CO\cdot CH_3$.

—3·25 Grams of *o*-chloroaniline were dissolved in 8·25 c.c. of fuming hydrochloric acid and 40 c.c. of water, and diazotised with 1·75 grams of sodium nitrite in 8 c.c. of water. The diazo-solution was added to 3·8 grams of *p*-acetylaminophenol and 10 grams of sodium acetate in 100 c.c. of well-cooled alcohol. The azo-compound began to separate immediately; after crystallisation from glacial acetic acid, red needles melting at 199—200° were obtained:

0·1532 gave 19·5 c.c. N_2 at 25° and 761 mm. N=14·5.

$C_{14}H_{12}O_2N_3Cl$ requires N=14·5 per cent.

m′-*Chloro*-m-*acetylamino*-o-*hydroxyazobenzene*, obtained in a similar manner, formed orange-brown needles melting at 206—207° after crystallisation from alcohol:

0·1537 gave 19·1 c.c. N_2 at 18° and 769·5 mm. N=14·5.

$C_{14}H_{12}O_2N_3Cl$ requires N=14·5 per cent.

p′-*Chloro*-m-*acetylamino*-o-*hydroxyazobenzene* separates from glacial acetic acid in coarse, yellow needles, melting at 217—218°:

0·1554 gave 19·6 c.c. N_2 at 23° and 761 mm. N=14·5.

$C_{14}H_{12}O_2N_3Cl$ requires N=14·5 per cent.

o′-*Bromo*-m-*acetylamino*-o-*hydroxyazobenzene* was obtained from glacial acetic acid in small, yellow prisms, melting and decomposing at 206—208·5°:

0·1835 gave 0·3388 CO_2 and 0·0632 H_2O. C=50·35; H=3·8.
0·1842 ,, 19·3 N_2 at 20° and 762·4 mm. N=12·2.

$C_{14}H_{12}O_2N_3Br$ requires C=50·3; H=3·6; N=12·57 per cent.

m′-*Bromo*-m-*acetylamino*-o-*hydroxyazobenzene* crystallises from glacial acetic acid in reddish-brown needles melting at 217—218°:

0·1695 gave 18·1 c.c. N_2 at 16° and 758·5 mm. N=12·5.

$C_{14}H_{12}O_2N_3Br$ requires N=12·57 per cent.

p′-*Bromo*-m-*acetylamino*-o-*hydroxyazobenzene* crystallises from glacial acetic acid in brown plates melting at 222—223°:

0·2715 gave 30·0 c.c. N_2 at 23° and 749·5 mm. N=12·5.

$C_{14}H_{12}O_2N_3Br$ requires N=12·57 per cent.

o′-*Nitro*-m-*acetylamino*-o-*hydroxyazobenzene* separates from glacial acetic acid in dark red crystals melting at 216—217°. It is somewhat soluble in alcohol, sparingly so in acetone, benzene, or chloroform:

0·1368 gave 21·6 c.c. N_2 at 21° and 770 mm. N=18·5.

$C_{14}H_{12}O_4N_4$ requires N=18·66 per cent.

m′-*Nitro*-m-*acetylamino*-o-*hydroxyazobenzene* crystallises from glacial acetic acid in reddish-brown needles melting at 231—233°:

0·2527 gave 39·5 c.c. N_2 at 16° and 760 mm. N = 18·44.
$C_{14}H_{12}O_4N_4$ requires N = 18·66 per cent.

p′-*Nitro*-m-*acetylamino*-o-*hydroxyazobenzene* melts at 235°; it crystallises from nitrobenzene in red needles:

0·1916 gave 0·3934 CO_2 and 0·0729 H_2O. C = 56·1; H = 4·2.
0·1416 „ 21·6 c.c. N_2 at 11° and 769 mm. N = 18·34.
$C_{14}H_{12}O_4N_4$ requires C = 56·0; H = 4·0; N = 18·66 per cent.

The alkaline solution of this compound is violet.

p-Benzoylaminophenol has also been examined with regard to its capacity of coupling with diazonium salts. Some confusion exists as to the melting point of this compound; it was given by Hübner (*Annalen*, 1882, **210**, 378) as 227°, by Smith (*Ber.*, 1891, **24**, 4042) as 205°, whilst Reverdin and his co-workers assign melting points of 214—215° and 233—234° to *p*-benzoylaminophenol and *p*-benzoylaminophenyl benzoate respectively (*Ber.*, 1904, **37**, 4452; 1906, **39**, 125). Subsequently Tingle and Williams (*Amer. Chem. J.*, 1907, **37**, 51) have ascribed to the monobenzoyl compound a melting point of 227·5°, substantially agreeing with Hübner.

Reverdin has recorded essentially correct melting points, as is shown by the following experiment.

10·9 Grams of *p*-aminophenol were dissolved in a solution of 6 grams of sodium hydroxide in 100 c.c. of water; 12·85 grams of benzoyl chloride were slowly added with continual stirring, the precipitate was collected and washed with cold dilute alkali, and crystallised from glacial acetic acid. The colourless crystals so obtained melted at 235°. The filtrate was acidified, the precipitate collected, and recrystallised from glacial acetic acid until the melting point (216—217°) was constant.

Substance melting at 216—217°:

0·3828 gave 21·9 c.c. N_2 at 13·5° and 747 mm. N = 6·7.
$C_6H_4(OH)\cdot NH\cdot C_7H_5O$ requires N = 6·6 per cent.

Substance melting at 235°:

0·2947 gave 11·4 c.c. N_2 at 15° and 741·5 mm. N = 4·4.
$C_6H_4(O\cdot C_7H_5O)\cdot NH\cdot C_7H_5O$ requires N = 4·4 per cent.

m-*Benzoylamino*-o-*hydroxyazobenzene*.—A solution made by diazotising 2·3 grams of aniline in 7 c.c. of concentrated hydrochloric acid and 20 c.c. of water with 1·72 grams of sodium nitrite dissolved in 8 c.c. of water was added to 5·3 grams of benzoylaminophenol and 10 grams of sodium acetate in 500 c.c. of alcohol, the whole being well cooled. The product of coupling separates from alcohol or glacial acetic acid in brown needles melting at 201°:

0·1663 gave 18·7 c.c. N_2 at 15° and 757 mm. N = 13·0.
$C_{19}H_{15}O_2N_3$ requires N = 13·2 per cent.

p′-*Nitro*-m-*benzoylamino*-o-*hydroxyazobenzene* separates as a red precipitate when *p*-nitrobenzenediazonium chloride is coupled with *p*-benzoylaminophenol. It is obtained from glacial acetic acid in lustrous, stout, dark needles, melting at 267—268°. The alkaline solution is violet:

0·1323 gave 17·9 c.c. N_2 at 12° and 731 mm. N = 15·6.
$C_{19}H_{14}O_4N_4$ requires N = 15·5 per cent.

We desire to tender our thanks to the Government Grant Committee of the Royal Society for a grant, by which some of the expenses of this investigation have been defrayed.

East London College,
University of London.

CLXXXIX.—*The Absorption Spectra of Nitro-compounds.*

By John Theodore Hewitt, Frank George Pope, and Winifred Isabel Willett.

The very considerable displacement of the absorption band produced when alkali is added to a solution of a nitrophenol has been held to depend on the formation of a quinonoid salt (Armstrong, Baly, Hantzsch, Hewitt), and whilst, so far, chemical evidence in favour of such structural change has not been offered to any great extent, the greater displacement of the band in the case of the nitrophenols as compared with the phenols themselves or their alkyl- or halogen-substituted derivatives certainly points in the direction of salt-formation following different courses in the two cases.

Baly, Tuck, and Marsden (Trans., 1910, **97**, 571) have re-examined the subject of the absorption spectra of the nitro-derivatives of aromatic compounds, and in their later paper do not confirm the views put forward by Baly, Stewart, and Edwards (Trans., 1906, **89**, 514). Instead of attributing the change in absorption to change in structure, it is pointed out that the absorption spectra of phenol and sodium phenoxide differ, the band shifting towards the red on salt-formation. Baly, Tuck, and Marsden (*loc. cit.*, p. 580) state that "the absorption spectrum of phenol shows a band with its head at $1/\lambda = 3680$, whilst sodium phenoxide shows a band with head at $1/\lambda = 3420$. In nitrophenols, therefore, the isorropesis is between the free period of the nitro-group and a residue with bands at $1/\lambda = 3680$, whilst in the sodium nitrophenoxides the isorropesis is between the nitro-group and a residue with a band at $1/\lambda = 3420$. Clearly, therefore, the absorption of the latter compound should be much nearer the red."

This is actually the case, but no explanation is offered of the fact that the displacement of the absorption band is greater when the nitro-group is present than when it is absent; and the question has still to be decided as to whether the greater difference between the spectra of a nitrophenol and its salts as compared with the unsubstituted phenol and its salts is qualitative, and due to a "specific"* action of the nitro-group, or accompanies a change of structure involving in this case a quinonoid configuration for the salt.

Quinonoid change is possible in the case of salt formation from a nitrophenol, impossible for phenol itself. This is no proof that quinonoid rearrangement actually takes place; it, however, draws attention to a possible connexion between change in constitution and change in absorption.

The most satisfactory way of dealing with the problem would be to examine such a salt as sodium nitrophenoxide and demonstrate that (i) reactions associated with the group $\vdots C \cdot ONa$ are absent; (ii) the nitro-group differs in its behaviour from that observed in compounds which undoubtedly contain the group $\vdots C \cdot NO_2$.

Another way of obtaining evidence is to show that the nitro-group only produces a large displacement of the absorption band on salt-formation in those cases where a quinonoid rearrangement is possible; if this is precluded by the constitution of the compound the displacement of the absorption towards the red end of the spectrum on salt-formation is of the same order as that observed with unsubstituted compounds or substances containing halogen in place of the nitro-group.

The purely chemical methods are at present engaging our attention; meanwhile we wish to record certain results obtained for the absorption spectra of carboxylic acids and their salts, which show that the nitro-group in itself has no abnormal effect in diminishing oscillation frequency when an acid is converted into its salt.

In Fig. 1 the curves for the absorption spectra of benzoic acid and its *p*-bromo- and *p*-nitro-derivatives, both in alcoholic solution and in presence of an excess of sodium hydroxide, are given.

The absorption is displaced towards the red end of the spectrum

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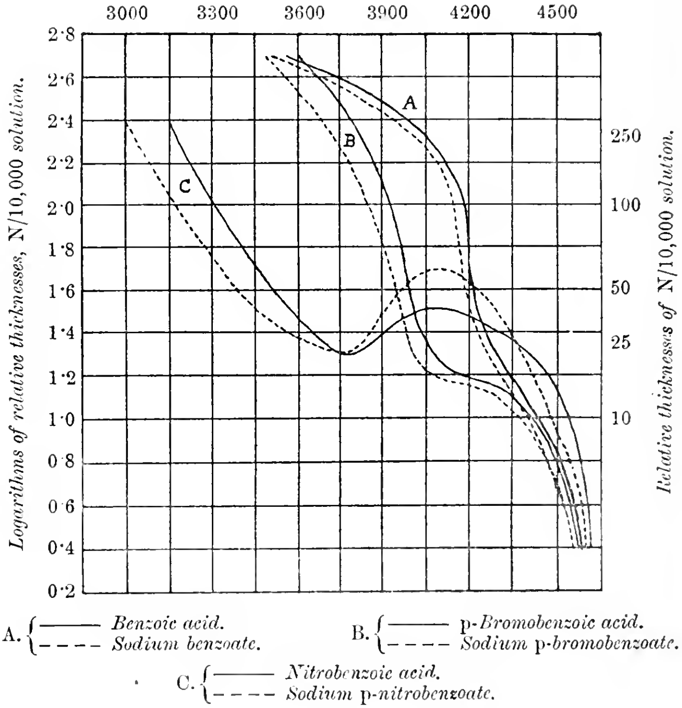
* For want of a better term.—J. T. H.

in each case on salt-formation, and the extent of the displacement is much the same for each acid. On chemical grounds it must be assumed that the changes:

$$C_6H_5{\cdot}CO_2H \longrightarrow C_6H_5{\cdot}CO_2Na$$
$$C_6H_4Br{\cdot}CO_2H \longrightarrow C_6H_4Br{\cdot}CO_2Na$$
$$NO_2{\cdot}C_6H_4{\cdot}CO_2H \longrightarrow NO_2{\cdot}C_6H_4{\cdot}CO_2Na$$

are of the same nature, and the spectroscopic results give no reason to doubt the correctness of this view.

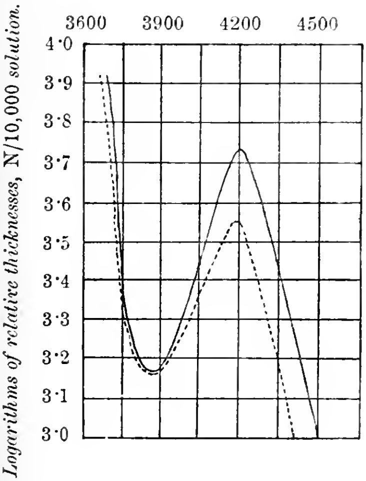
FIG. 1.



In the case of derivatives of phenylacetic acid and its ester and nitrile, the possibility of a different type of salt-formation is introduced with certain para-substituents. The hydrogen atoms of the methylene group exhibit a certain amount of reactivity; in the case of ethyl phenylacetate, displacement of hydrogen by alkyl groups may be effected, whilst the nitrile is even more reactive. If, however, in the case of the ester and of the nitrile, displacement of hydrogen by metal does take place when alkali is added to the alcoholic solution, either the number of molecules converted into salt is relatively small (that is, the salt is very largely hydrolysed), or otherwise the metallic derivative produced is of the same or very similar type to the original compound. In Fig. 2 the absorption spectrum of alcoholic phenylacetonitrile alone and in presence of alkali (excess) is given; Fig. 3 compares the absorptions of phenylacetic acid and its sodium salt. The alteration produced by the salt-formation is slight in each case, and not dissimilar in extent to the change accompanying salt-formation from benzoic acid and its derivatives. Quinonoid change is excluded, and no great change in the absorption is produced.

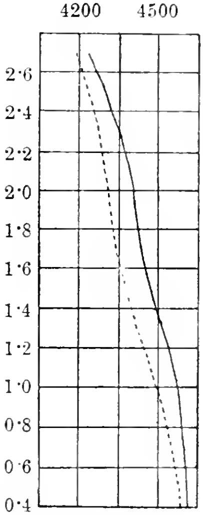
With the introduction of a *p*-nitro-group, the possibility of the metallic derivative assuming a quinonoid structure has to be considered. The metallic derivatives of *p*-nitrophenylacetonitrile and of ethyl *p*-nitrophenylacetate might be derived from the parent substances in the following manner:

FIG. 2.



—— *Phenylacetonitrile in alcoholic solution.*
--- ,, ,, ,, +NaOH.

FIG. 3.

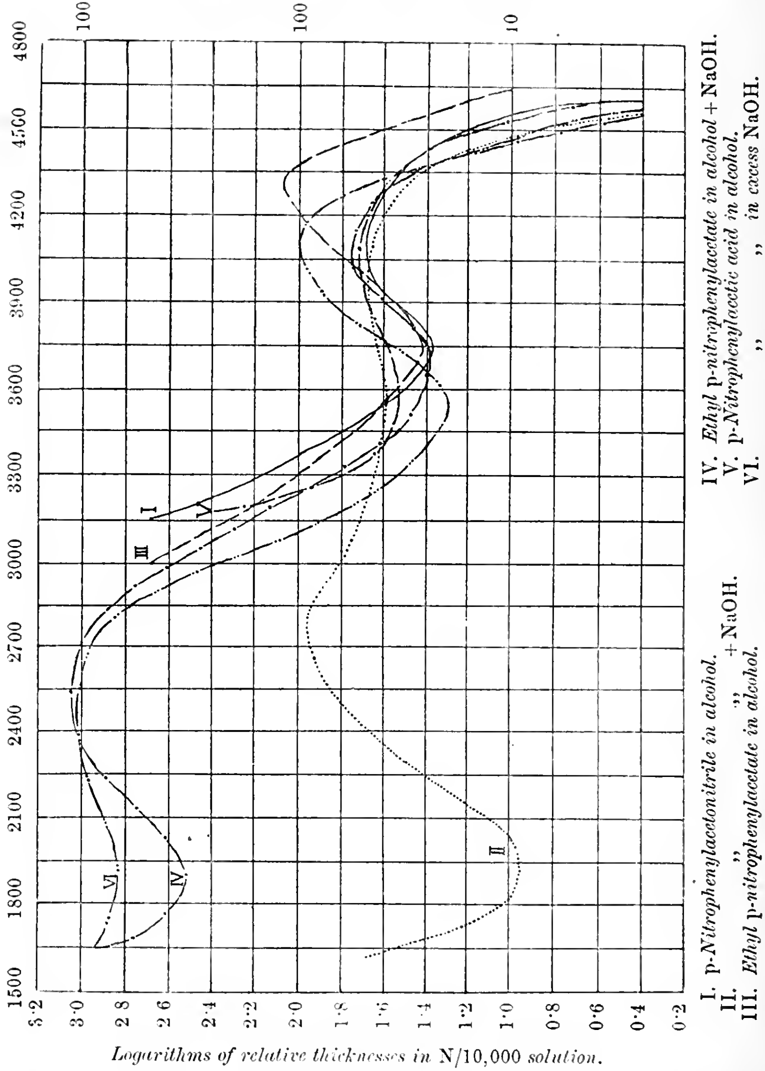


—— *Phenylacetic acid.*
--- *Sodium phenylacetate.*

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN \longrightarrow NaNO_2{:}C_6H_4{:}CH{\cdot}CN$$
$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5 \longrightarrow NaNO_2{:}C_6H_4{:}CH{\cdot}CO_2{\cdot}C_2H_5,$$

and with the greater length of chain of conjugated unsaturated linkings a very marked displacement of the absorption might be expected. As a matter of fact, a very intense purple colour is developed on addition of alkali to an alcoholic solution of the nitrile; the colour development is not so great, although quite striking, in the case of the ester. Since the carbethoxy- is less acidifying than the nitrile group, a greater hydrolysis of the sodium

FIG. 4.



derivative of the ester as compared with that of the nitrile is to be expected. The absorption spectra are recorded in Fig. 4, and are compared with that of nitrophenylacetic acid in alcoholic solution and in presence of a large excess of alkali.

Respecting the absorption spectra of the acid and its sodium salt, a great difference is not to be expected. The $\cdot CO_2Na$ group cannot have any very pronounced negative effect on the molecule, and a salt of the type

$$NaNO_2\colon C_6H_4\colon CH\cdot CO_2Na$$

can only exist in very small quantity; it would undergo nearly complete hydrolysis. With considerable excess of sodium hydroxide, it might be expected that small quantities of such a dibasic salt would exist side by side with larger quantities of the normal sodium *p*-nitrophenylacetate,

$$NO_2\cdot C_6H_4\cdot CO_2Na,$$

and the absorption spectra point to this conclusion being correct. The band due to the normal configuration is less persistent than that obtained with equimolecular concentration of the free acid, but the oscillation frequency is practically unaltered. At the same time, a shallow band of very nearly the same oscillation frequency as that observed in the sodium derivative of *p*-nitrophenylacetonitrile and ethyl *p*-nitrophenylacetate has made its appearance. The experimental result is, in fact, quite consistent with the deduction drawn from theoretical conclusions.

We desire to record our thanks to the Research Committee of the East London College for a grant, by which the expenses of this investigation have been defrayed.

East London College,
University of London.

CXC.—*Harmine and Harmaline. Part I.*

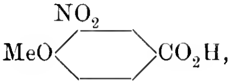
By William Henry Perkin, jun., and Robert Robinson.

The seeds of *Peganum harmala*, a plant which grows wild on the Steppes of South Russia and in India, contain two closely related alkaloids, harmine, $C_{13}H_{12}ON_2$, and harmaline, $C_{13}H_{14}ON_2$ (Goebel, *Annalen*, 1841, **38**, 363; Fritzsche, *ibid.*, 1847, **64**, 360), which on account of their unusual and interesting properties have been the subject of repeated investigation at the hands of chemists, among whom Otto Fischer and his co-workers must be specially mentioned. In spite, however, of the fact that so much work has been done on the subject, the results have so far been insufficient to afford a clue to the constitutions of these remarkable substances, and it was with the object of obtaining further information bearing on this point that the present investigation was commenced in these laboratories some four years ago. Whilst it will not be necessary at this stage to give a detailed account of the work which has already been accomplished in connexion with the investigation, and especially with the degradation of these alkaloids, such of the facts as have a direct bearing on the question of constitution will need to be mentioned. Harmaline, $C_{13}H_{14}ON_2$, differs from harmine, $C_{13}H_{12}ON_2$, by two atoms of hydrogen, and that the two alkaloids are closely related and that harmaline is dihydroharmine is indicated by the fact that harmaline may be converted into harmine by oxidation with dilute nitric acid. The reverse change has, however, not been effected, since harmine, on reduction with sodium and alcohol, yields tetrahydroharmine, $C_{13}H_{16}ON_2$, a substance which is also produced from harmaline by treatment with zinc dust and hydrochloric acid (O. Fischer, *Ber.*, 1889, **22**, 637). Harmaline crystallises from alcohol in large, glistening, colourless prisms, and melts and decomposes at about 250°; it combines readily with one equivalent of an acid, yielding pale yellow, crystalline salts, such as the hydrochloride, $C_{13}H_{14}ON_2,HCl$, and the platinichloride, $(C_{13}H_{14}ON_2,HCl)_2PtCl_4$.

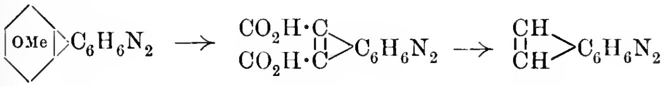
It is a secondary base, since, on treatment with methyl iodide, it is converted in the first place into methylharmaline, $C_{13}H_{13}ON_2Me$, and then into methylharmaline methiodide, $C_{13}H_{13}ON_2Me_2I$; harmaline is also converted into acetylharmaline, $C_{13}H_{13}ON_2Ac$, by treatment with acetic anhydride and sodium acetate (O. Fischer and E. Täuber, *Ber.*, 1885, **18**, 405; 1897, **30**, 2483). Both harmaline and harmine are optically inactive. Harmine, $C_{13}H_{12}ON_2$, crystallises from alcohol in colourless needles, melts at 257°, and yields salts, such as the hydrochloride, $C_{13}H_{12}ON_2,HCl,2H_2O$, and the sulphate, $C_{13}H_{12}ON_2,H_2SO_4,H_2O$, which are colourless, but their dilute solutions exhibit a striking deep blue fluorescence. Like harmaline, harmine is converted, by the action of methyl iodide, first into methylharmine, $C_{13}H_{11}ON_2Me$, and then into methylharmine methiodide, $C_{13}H_{11}ON_2Me_2I$, and is therefore a secondary base, and since it contains one methoxy-group, its formula may be developed to $MeO\cdot C_{12}H_8N(NH)$.

When harmine (or harmaline) is oxidised by chromic acid it undergoes a very important change and is converted into harminic acid, $C_8H_6N_2(CO_2H)_2$, which, since it yields a phthalein when heated with resorcinol and sulphuric acid, is evidently an *o*-dicarboxylic acid (O. Fischer and E. Täuber, *Ber.*, 1885, **18**, 403).

On heating under diminished pressure, this acid is decomposed with elimination of carbon dioxide and formation of *apo*harmine-carboxylic acid, $C_8H_7N_2 \cdot CO_2H$, and, on further heating, the remaining carboxyl group is removed and *apo*harmine, $C_8H_8N_2$, is obtained (O. Fischer and E. Täuber, *loc. cit.*, p. 403). Since O. Fischer (*Festschrift*, Erlangen, Abstr., 1901, i, 405; compare Fischer and Boesler, *Ber.*, 1912, **45**, 1934) has shown that harmaline yields *m*-nitroanisic acid,



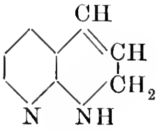
on treatment with nitric acid and *apo*harmine does not contain the methoxy-group, it follows that, during the oxidation of harmine, the methoxyphenyl ring is destroyed, giving place to two carboxyl groups, and the harminic acid thus produced then yields *apo*harmine by the elimination of these two carboxyl groups, a series of decompositions which may be represented thus:



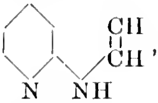
Harmine. Harminic acid. *apo*Harmine.

It thus became quite clear that, if the constitution of *apo*harmine could be elucidated, this would supply the key to the constitutions of harmine and harmaline, and open the way to the possible synthesis of these substances. *apo*Harmine is a colourless, crystalline substance, which melts at 183°, and yields salts such as the hydriodide, $C_8H_8N_2,HI,H_2O$, with one equivalent of the acid.

It is a secondary base, and is converted by nitric acid into nitro-*apo*harmine, $C_8H_7(NO_2)N_2$, but beyond these facts no information was available at the time the experiments described in the present communication were commenced, which afforded any clue to its constitution. In considering the many possible alternatives, we soon found that the assumption that all the carbon and nitrogen atoms take part in the actual structure of rings and that *apo*harmine has, for example, some such constitution as

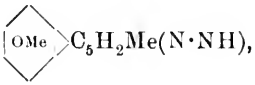


presented great difficulties. On the other hand, if it is assumed that *apo*harmine contains a methyl group united to some such skeleton as that obtained by the fusion of a pyridine with a pyrrole nucleus, as in the case of 8-pyrindole,*



for example, many of these difficulties at once disappeared.

Our first endeavour, therefore, was to demonstrate the presence of a methyl group, and, after several unsuccessful experiments, we ultimately discovered that harmine condenses readily with aldehydes, and yields with benzaldehyde, for example, *benzylideneharmine*, $C_{12}H_9ON_2\cdot CH{:}CH\cdot C_6H_5$, and with *p*-nitrobenzaldehyde, p-*nitrobenzylideneharmine*, $C_{12}H_9ON_2\cdot CH{:}CH\cdot C_6H_4\cdot NO_2$. When benzylideneharmine, dissolved in aqueous pyridine, is oxidised with permanganate, it is converted into *norharminecarboxylic acid*, $C_{12}H_9ON_2\cdot CO_2H$, which, on heating with glycerol, loses carbon dioxide, and yields *norharmine*, $C_{12}H_{10}ON_2$, a substance possessing properties very similar to those of harmine, and this series of decompositions clearly indicates that harmine contains a methyl group. Furthermore, the fact that this methyl group condenses with aldehydes suggests that it is in a similar position to the methyl group in quinaldine, which also exhibits this behaviour, and that therefore the methyl group in harmine is in the α-position with respect to one of the nitrogen atoms, and this view is confirmed by the fact that norharminecarboxylic acid develops a brownish-red coloration when ferrous sulphate is added to its aqueous solution, a reaction characteristic of carboxylic acids in which the carboxyl group occupies the α-position. These considerations lead to the conclusion that harmine has the structure represented by the formula:



that is to say, it is the methylmethoxybenzo-derivative of a base, $C_7H_6N_2$, which may be considered as the parent substance of harmine, and for which we propose the name apo*harmyrine.*

The properties, and especially the stability of *apo*harmyrine and its derivatives, clearly indicate that these substances contain two closed nuclei. If, then, an attempt is made to devise a formula for *apo*harmyrine, we find at once that a possible structure cannot be obtained by fusing a six- and a five-ring together with the aid of

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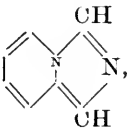
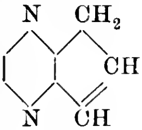
* For an explanation of the nomenclature of this substance and the other substances discussed in this paper, see p. 1787.

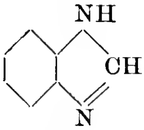
one or both of the nitrogen atoms, since this would lead to some such expression as:



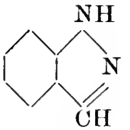
which cannot contain the >NH-group known to be present in *apo*harmine, and therefore in *apo*harmyrine. Three possibilities remain for discussion, namely, (I) both nitrogen atoms are in the six-membered ring, (II*a* and II*b*) both nitrogens are in the five-membered ring, or, each ring contains a nitrogen atom:



(I.)



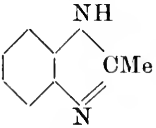
(II*a*.)



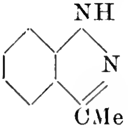
(II*b*.)

A formula such as that represented by (I) is not possible, because in the first place it does not contain an >NH group, and secondly, a derivative of *cyclo*pentadiene of this kind would not resist the action of oxidising agents in the way *apo*harmyrine does.

Schemes II*a* and II*b* are also impossible, because, if *apo*harmyrine had either of these formulæ, *apo*harmine would either be identical with methylbenziminazole (III) or with methylindazole (IV), which

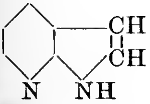


(III.)

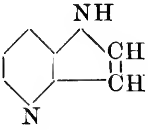


(IV.)

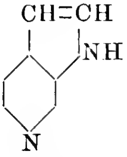
is not the case. The only alternative is to assume that each ring contains a nitrogen atom, and *apo*harmyrine must then consist of fused pyrrole and pyridine nuclei, and it is clear that this fusion may take place in four different ways, giving rise to the following four expressions (for nomenclature see p. 1787):



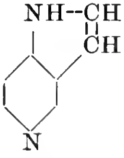
(V.)
8-Pyrindole.



(VI.)
5-Pyrindole.



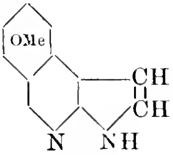
(VII.)
7-Pyrindole.



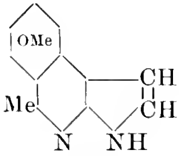
(VIII.)
6-Pyrindole.

Although we are not yet in a position to select definitely one of these alternatives, expression (V) seems to us to be the most probable for the following reasons: It has already been mentioned (p. 1777) that harmaline yields *m*-nitroanisic acid when it is oxidised with nitric acid, and this would seem to indicate that the anisole nucleus is attached to two carbon atoms in the *o*-position, thus: $MeO\cdot C_6H_3<^{C}_{C}$, and that the point of fusion of the anisole and *apo*harmyrine nuclei is in the pyridine portion of the molecule and in the 2:3-position relative to the nitrogen atom.

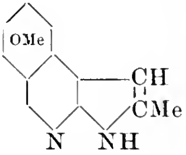
Confirmatory evidence of this view is to be found in the fact that harminic acid, in the formation of which the anisole nucleus is destroyed, does not give a coloration with ferrous sulphate, and therefore does not contain a carboxyl group in the *α*-position with respect to a nitrogen atom. These considerations rule out structures (VII) and (VIII), since they do not contain a 2:3-position on which to fuse the anisole nucleus. Of the remaining structures we prefer (V) because of its close analogy to benziminazole, the methyl derivative of which is in many ways strikingly similar in properties to *apo*harmine, and also because the relative positions of the nitrogen atoms afford an explanation of the fact that *apo*harmine and its derivatives are monacid bases. If expression (V) is accepted as representing *apo*harmyrine, then the formula of norharmine (p. 1778) must be (IX), and that of harmine itself either (X) or (XI):



(IX.)



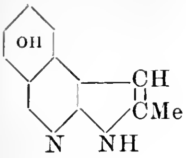
(X.)



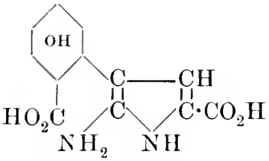
(XI.)

Now O. Fischer and E. Täuber (*Ber.*, 1885, **18**, 402) have shown that harmine, $C_{13}H_{12}ON_2$, is decomposed by heating with hydrochloric acid at 140° with hydrolysis of the methoxy-group and formation of the corresponding phenol, $C_{12}H_{10}ON_2$, to which they give the name harmol.

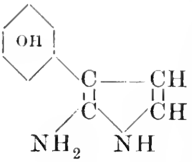
When this phenol is fused with potassium hydroxide, it suffers hydrolysis and oxidation, and yields harmolic acid, $C_{12}H_{10}O_5N_2$, and this, on distillation, loses two molecules of carbon dioxide with formation of a phenolic base, $C_{10}H_{10}ON_2$. It seems to us that this series of changes can only be explained on the assumption that formula (XI) represents the constitution of harmine, and the formation of harmolic acid and the phenolic bases follows then in a simple manner in accordance with the scheme:



Harmol.



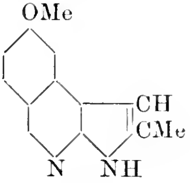
Harmolic acid.



Phenolic base.

Finally, if this explanation is correct, the position of the hydroxy-group is probably para to the readily eliminated carboxyl group, a conclusion which is in agreement with the formation of *m*-nitro-anisic acid by the oxidation of harmaline with nitric acid.

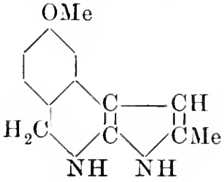
It follows, therefore, that the most probable expression for harmine is the formula:



Harmine.

and this *iso*quinoline structure will be found to explain in a simple manner all the properties and decompositions of this substance.

The constitution of harmaline or dihydroharmine may be readily deduced from the above formula for harmine, and is most probably



Harmaline.

the two extra hydrogen atoms serving to reduce the pyridine nucleus of the *iso*quinoline portion of the molecule.

Quite recently (*Ber.*, 1912, **45**, 1930) O. Fischer and W. Boesler have pointed out an interesting difference in the behaviour of harmine and harmaline towards diazonium salts; harmaline combines readily with two molecules of a diazonium salt with the formation of bisazo-derivatives, whereas harmine does not react. The formulæ which we propose for harmine and harmaline appear to offer a satisfactory explanation for this difference in behaviour. Just as the fusion of the two benzene nuclei in naphthalene, or the benzene and pyridine nuclei in quinoline and *iso*quinoline greatly modifies the properties of the separate rings, so it may be assumed that the corresponding fusion of the pyridine and pyrrole nuclei in the case of harmine brings about a fundamental change in the characteristic properties of each of these rings *; thus harmine is neither a true pyridine nor a true pyrrole derivative, and it is therefore not surprising that it does not exhibit the characteristic property possessed by pyrrole of combining with diazonium salts to form azo- and bisazo-derivatives.

In the case of harmaline the pyridine ring is partly reduced, and thus loses its influence on the pyrrole ring, so that that ring becomes again capable of combining with diazonium salts in a manner similar to pyrrole itself. The bisazo-derivatives of harmaline described by Fischer and Boesler are probably produced by substitution, both in the $\cdot CH\colon$ group of the pyrrole nucleus and the methyl group in the α-position. Other reactions of harmaline are in complete agreement with this view, thus, for example, harmaline may be nitrated in the anisole nucleus, whereas the nitration of harmine has not yet been accomplished, and this difference in behaviour is obviously due to some difference in that portion of the molecule adjacent to the anisole nucleus. When harmaline is digested in methyl-alcoholic solution with benzaldehyde, it is converted quantitatively into *benzylidenediharmaline*,

$$(C_{12}H_{11}ON_2\cdot CH_2)_2CH\cdot C_6H_5$$

(p. 1786), and in this respect it again differs in a marked manner from harmine, which, as has already been pointed out (p. 1778), condenses with much less readiness with benzaldehyde and in molecular proportions, yielding benzylideneharmine,

$$C_{12}H_9ON_2\cdot CH\colon CH\cdot C_6H_5.$$

It is of interest to note that the condensation of harmaline with aldehydes proceeds in the same direction as in the case of α-methylindole, since this substance also reacts very readily with aldehydes to yield derivatives, in the formation of which two molecules of the base combine with one molecule of the aldehyde with the loss of one molecule of water (v. Walther and Clemen, *J. pr. Chem.*, 1900, [ii], **61**, 274).

EXPERIMENTAL.

Benzylideneharmine, $C_{12}H_9ON_2\cdot CH\colon CH\cdot C_6H_5$.

In order to prepare this condensation product, harmine (10 grams) is boiled with freshly distilled benzaldehyde (50 c.c.) for an hour, during which the liquid becomes yellowish-brown and water is eliminated.

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* We are at present engaged in attempts to synthesise substances containing pyridine and pyrrole rings fused in different positions in order to determine what influence such fusion has on the specific properties of these rings.

The product is then cooled somewhat, diluted with alcohol (70 c.c.), and concentrated hydrochloric acid (35 c.c.) added, when a mass of yellow needles separates from the solution. These consist of the hydrochloride of benzylideneharmine, and, after collecting, washing with alcohol and drying, the substance is sufficiently pure for most purposes, such as, for example, the preparation of norharminecarboxylic acid (p. 1784).

A portion of the salt was decomposed by dilute aqueous-alcoholic ammonia, and the resulting *benzylideneharmine* collected, dried, and recrystallised from alcohol, from which it separated either in very pale yellow prisms or in needles, according to the concentration of the solution. It melts at 191—192°, and its solutions in all neutral solvents exhibit an intense violet-blue fluorescence. The substance itself, as well as its solutions, acquires a yellow colour on exposure to light:

0·1102 gave 0·3226 CO_2 and 0·0536 H_2O. C=79·7; H=5·4.
0·1062 ,, 0·3111 CO_2 ,, 0·0550 H_2O. C=79·9; H=5·7.
$C_{20}H_{16}ON_2$ requires C=80·0; H=5·3 per cent.

The salts of benzylideneharmine are sparingly soluble in water; the *nitrate* and *sulphate*, for example, are precipitated in yellow needles on the addition of nitric or sulphuric acids respectively to the solution of the base in dilute acetic acid, and of these salts the sulphate is the more sparingly soluble.

The Hydrochloride.—In order to prepare a pure specimen of this salt, the crude hydrochloride, obtained in the manner just described, was recrystallised from alcohol, when it separated in stout, yellowish-brown needles, which are sparingly soluble in alcohol or water.

The substance appeared to contain solvent of crystallisation, and the specimen for analysis was therefore dried at 110°, when it was found to be anhydrous:

0·1314 gave 0·0548 AgCl. Cl=10·2.
$C_{20}H_{16}ON_2,HCl$ requires Cl=10·4 per cent.

p-*Nitrobenzylideneharmine*, $C_{12}H_9ON_2{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$.—This substance is readily produced when small quantities of harmine and *p*-nitrobenzaldehyde are cautiously heated in test-tubes until the reaction, as indicated by the water eliminated, is complete.

The product is dissolved in hot alcohol, when the red solution, on cooling, furnishes the condensation product as a brick-red, crystalline precipitate. The substance is very sparingly soluble, and may best be recrystallised from boiling ethyl acetate, from which it separates in red needles melting at 266°:

0·1062 gave 0·2701 CO_2 and 0·0419 H_2O. C=69·3; H=4·4.
$C_{20}H_{15}O_3N_3$ requires C=69·6; H=4·3 per cent.

Faintly alkaline permanganate oxidises this substance with the formation of norharminecarboxylic acid (see below), but the yield is not good.

C-*Benzylharmine*, $C_{12}H_9ON_2\cdot CH_2\cdot CH_2\cdot C_6H_5$.

The reduction of benzylideneharmine presented, at first, some experimental difficulties, but ultimately the following method was found to give good results. Benzylideneharmine hydrochloride (5 grams) and sodium acetate (2 grams), dissolved in glacial acetic acid, are boiled with zinc dust (5 grams) until the solution is completely decolorised. The liquid is diluted with water, filtered, and mixed with sufficient potassium hydroxide to dissolve the precipitated zinc hydroxide. The milky liquid gradually clarifies, and deposits a rather viscid, colourless substance, which is collected and dissolved in alcohol. The addition of hydrochloric acid to the alcoholic solution causes the separation of a crystalline hydrochloride, which is collected, decomposed with cold aqueous ammonia, and the base repeatedly recrystallised from methyl alcohol, in which it is sparingly soluble:

0·1365 gave 0·3973 CO_2 and 0·0764 H_2O. C=79·4; H=6·2.

$C_{20}H_{18}ON_2$ requires C=79·5; H=6·0 per cent.

C-*Benzylharmine* separates from methyl alcohol in well-defined, colourless, rectangular prisms, and melts at 138°. It is characterised by this low melting point and by the fact that it is readily soluble in common solvents, such as alcohol, but, in other respects, it resembles the parent alkaloid. It yields sparingly soluble salts; the *hydrochloride*, for example, crystallises from water in slender needles, and its solutions exhibit a blue fluorescence.

Norharminecarboxylic Acid, $C_{12}H_9ON_2\cdot CO_2H$.

This acid was first obtained by the oxidation of the solution of benzylideneharmine sulphate in hot, very dilute aqueous acid with permanganate, but the yields were always unsatisfactory.

After a long series of comparative experiments, the following process of oxidation of the base itself in pyridine solution was found to work extremely well, and this method will probably be found of value in the case of the oxidation of other sparingly soluble substances. Benzylideneharmine hydrochloride (5 grams), dissolved in pyridine (100 c.c. of Kahlbaum's "Pyridine I.") and an equal volume of water, is gradually mixed with a cold saturated aqueous solution of potassium permanganate (300 c.c.), when oxidation takes place rapidly. After remaining for three-quarters of an hour, methyl alcohol is added to reduce the excess of permanganate; the solution is then treated with sodium carbonate (1 gram), considerably diluted with water, boiled, and filtered. The pale yellow filtrate and washings of the manganese precipitate are evaporated nearly to dryness, and rendered acid to Congo-paper by means of hydrochloric acid. This causes the precipitation of the sparingly soluble hydrochloride of norharminecarboxylic acid in the form of yellow needles; sodium acetate is then added in sufficient quantity to neutralise the hydrochloric acid, and the pale yellow precipitate, which now consists of the free acid, is collected and washed with hot water. The substance is then dissolved in hot glacial acetic acid, when, on cooling, stout, glistening, yellow needles separate, which were found to consist of the *acetate* of *norharminecarboxylic acid*:

0·0980 gave 0·2126 CO_2 and 0·0422 H_2O. C = 59·2; H = 4·8.

$C_{13}H_{10}O_3N_2,C_2H_4O_2$ requires C = 59·6; H = 4·6 per cent.

On heating at 100° the crystals of this acetate fall to a yellow powder, which consists of the acid itself, but this loss of acetic acid is better effected by trituration in a mortar with hot water, when the substance gradually assumes crystalline form in the shape of pale yellow, woolly needles. Owing to its very sparing solubility in neutral solvents, norharminecarboxylic acid could not be recrystallised, but when prepared as described above it melts at 258° with vigorous decomposition:

0·1127 gave 0·2645 CO_2 and 0·0409 H_2O. C = 64·0; H = 4·0.

$C_{13}H_{10}O_3N_2$ requires C = 64·5; H = 4·1 per cent.

The *hydrochloride* and *sulphate* of norharminecarboxylic acid are bright yellow, sparingly soluble salts, which crystallise in needles.

When the acid is treated with nitric acid, the yellow nitrate is first produced, but this slowly dissolves, the solution acquires an olive-green, and finally a bluish-green colour, and an almost colourless precipitate separates on dilution with water. The *sodium* and *potassium* salts are sparingly soluble in water, and crystallise from dilute solutions in colourless, woolly needles. When aqueous ferrous sulphate is added to the suspension of the acid in alcohol, a brownish-red coloration is developed, and this reaction, which is so characteristic of the α-carboxylic acids of the pyridine and quinoline series, clearly indicates that the carboxyl group in norharminecarboxylic acid occupies the α-position with respect to one of the nitrogen atoms (compare p. 1778).

Norharmine, $C_{12}H_{10}ON_2$.

Norharminecarboxylic acid does not lose carbon dioxide smoothly on heating in a vacuum, but the elimination of the carboxyl group may fortunately be quantitatively accomplished by heating the substance with glycerol. The acid (0·5 gram) is mixed with glycerol (5 c.c.), and heated in a test-tube in a sulphuric acid bath, when evolution of carbon dioxide commences at 170°, and the heating is continued until this has almost finished, the temperature being finally raised to 200°. On the addition of water, the new base separates as a colourless, crystalline precipitate, and is collected, dried, and recrystallised from benzene:

0·0883 gave 0·2346 CO_2 and 0·0413 H_2O. C=72·4; H=5·2.

$C_{12}H_{10}ON_2$ requires C=72·7; H=5·0 per cent.

Norharmine is readily soluble in hot alcohol, but sparingly so in benzene; it crystallises from the latter solvent in colourless needles melting at 218°, and may be sublimed almost without decomposition. Its salts are pale yellow, and, in dilute solution, exhibit intense blue fluorescence. The *hydrochloride* crystallises from fairly concentrated aqueous solutions in prisms, the *aurichloride* separates from alcohol in pale brown needles, and the *mercurichloride* crystallises from water in long, pale yellow needles. Like harmine, it slowly colours a pine shaving moistened with hydrochloric acid, but the brownish-violet tint so produced is very weak. Norharmine is readily oxidised by chromic acid in acetic acid solution, and the products of this action are being examined with the ultimate object of attempting to prepare nor*apo*harmine.

Benzylidenediharmaline, $(C_{12}H_{11}ON_2\cdot CH_2)_2CH\cdot C_6H_5$.

This substance is very readily obtained by boiling finely powdered harmaline (10 grams) with freshly distilled benzaldehyde (15 grams) and methyl alcohol (100 c.c.) in a reflux apparatus, when, in a few minutes, the condensation product commences to separate in heavy crystals.

After about half an hour, the product is filtered hot, the residue washed with methyl alcohol until free from dark-coloured mother liquor, and then dried. The yield is 10 grams, and a further small quantity is deposited when the mother liquors are concentrated and allowed to remain:

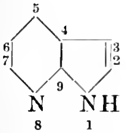
0·1296 gave 0·3666 CO_2 and 0·0764 H_2O. C=77·1; H=6·5.
0·1007 „ 9·8 c.c. N_2 at 17° and 748 mm. N=11·1.

$C_{33}H_{32}O_2N_4$ requires C=76·7; H=6·2; N=10·9 per cent.

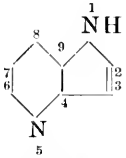
Benzylidenediharmaline is almost insoluble in methyl alcohol, methyl ethyl ketone, and most other organic solvents; it dissolves, however, comparatively readily in boiling pyridine, but apparently with some decomposition, and separates on cooling as an almost colourless, microcrystalline mass resembling powdered chalk. It darkens somewhat at about 230°, and melts and decomposes at about 245° to a dark reddish-brown liquid. It dissolves in sulphuric acid, with a lemon-yellow colour, and in acetic acid, yielding a deep yellow solution, and is not precipitated on the addition of water.

Nomenclature of Condensed Pyridine and Pyrrole Nuclei.

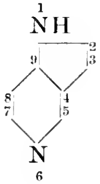
Substances containing condensed pyridine and pyrrole nuclei do not appear to be known, and, as their nomenclature presents some difficulties, the authors consulted Dr. Cain, who suggests that such substances may be called "pyrindoles," and that the position of the attachment of the rings will be clearly indicated by the following scheme *:



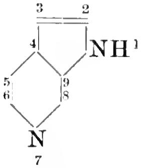
8-Pyrindole.



5-Pyrindole.

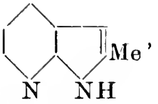


6-Pyrindole.

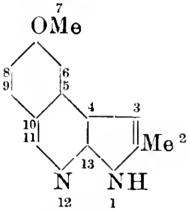


7-Pyrindole.

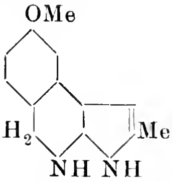
*apo*Harmine (p. 1778),



would then be 2-*methyl*-8-*pyrindole*, harmine (p. 1781),



7-*methoxy*-2-*methyl*-12-iso*quinindole*, and harmaline (p. 1781),



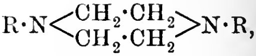
7-*methoxy*-2-*methyl*-11 : 12-*dihydro*-12-iso*quinindole*.

The University,
Manchester.

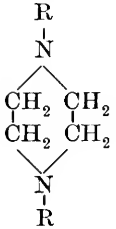
* It is essential that the carbon atoms common to both rings should be numbered, because, in the event of reduction, these become centres of possible substitution.

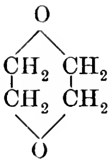
CXCI.—*The Relation between Residual Affinity and Chemical Constitution. Part III. Some Heterocyclic Compounds.*

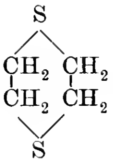
By Hans Thacher Clarke (1851 Exhibition Scholar).

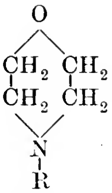
In Part II. of this series (Trans., 1911, **99**, 1927) it was shown that in the alkyl derivatives of piperazine,  $R\cdot N<\substack{CH_2\cdot CH_2\\CH_2\cdot CH_2}>N\cdot R$, the residual affinity of the nitrogen atoms, as interpreted from their chemical activity, was abnormally great. Further, it was stated that this abnormal reactivity was accompanied by optical exaltation. The study of heterocyclic compounds containing "unsaturated" atoms—to which a large amount of residual affinity is attributable—in the 1:4-positions in the saturated six-membered ring has now been extended so as to embrace all the remaining possible types of compound in which the unsaturated atoms are either oxygen, nitrogen, or sulphur. In addition to this, data bearing on the influence of ring-formation on certain physical properties (refractive power, dispersive power, and molecular volume) have been obtained.

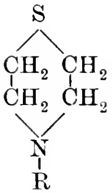
The types of compound principally examined in the experiments here described are the following:

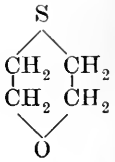

(I.) Piperazines.

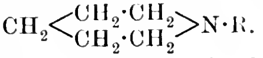

(II.) 1:4-Dioxan.


(III.) 1:4-Dithian.

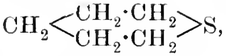

(IV.) Morpholines.


(V.) 1:4-Thiazans.


(VI.) 1:4-Thioxan.

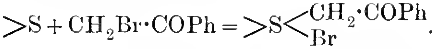
As was mentioned in Part II., the method of estimating the residual affinity of the piperazines, by a comparison of the velocity of addition of alkyl haloids with the corresponding open-chain compounds, was not entirely free from objection. In the present series of experiments the difficulty has been avoided by directly comparing the reactivities of the morpholines (IV) and the thiazans (V) with the corresponding derivatives of piperidine,  $CH_2<\substack{CH_2\cdot CH_2\\CH_2\cdot CH_2}>N\cdot R$. It may be taken that a minimal disturbance of conditions in the molecule occurs on the replacement of the central (γ) methylene group in piperidine by an atom of oxygen or sulphur, and that comparison of relative rates of addition is justifiable.

In the same way it has been found possible to compare 1:4-thioxan (VI) with pentamethylene sulphide,

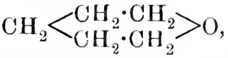


$$CH_2\left<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\right>S,$$

the estimation of residual affinity being interpreted from the rate of addition of bromoacetophenone:

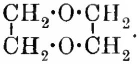


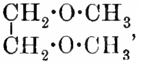
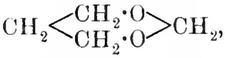
$$>S + CH_2Br\cdot COPh = >S\left<\begin{matrix}CH_2\cdot COPh\\ Br\end{matrix}\right..$$

Furthermore, the four standard systems—*cyclo*hexane, piperidine, pentamethylene oxide,  $CH_2\left<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\right>O$, and pentamethylene sulphide—have been utilised for the calculation of the physical properties, by ascertaining the changes in the molecular values on substituting a methylene group in *cyclo*hexane by an atom of oxygen or sulphur.

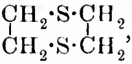
CHEMICAL PROPERTIES.

Compounds of Oxygen.

The central figure in this series is 1:4-dioxan, or diethylene-dioxide,  $\begin{matrix}CH_2\cdot O\cdot CH_2\\ | \qquad\quad |\\ CH_2\cdot O\cdot CH_2\end{matrix}$. Owing to the extreme weakness of the basic properties of ethereal oxygen in general, it has not been attempted to obtain more than qualitative evidence of chemical activity.

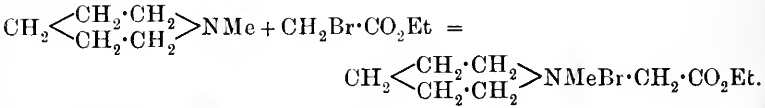
As was shown by Faworsky (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 741), Paternò and Spallino (*Atti R. Accad. Lincei*, 1907, [v], **16**, 187), and others, 1:4-dioxan readily yields salts with sulphuric acid, bromine, iodine, picric acid, and mercuric chloride. The open-chain compound, $\alpha\beta$-dimethoxyethane,  $\begin{matrix}CH_2\cdot O\cdot CH_3\\ |\\ CH_2\cdot O\cdot CH_3\end{matrix}$, on the other hand, behaves as a strictly neutral substance; and with the exception of 1:3-dioxan (trimethylenemethylal),  $CH_2\left<\begin{matrix}CH_2\cdot O\\ CH_2\cdot O\end{matrix}\right>CH_2$, which forms an unstable picrate and yields a crystalline double compound with mercuric chloride, none of the remaining compounds of oxygen here described appears to possess abnormal basic properties. From purely chemical evidence, therefore, the conclusion must be formed that the two oxygen atoms situated in the 1:4-positions in the cyclic system exert a mutual influence in the same way as the nitrogen atoms in the piperazines, with the effect of augmenting the basic function of the unsaturated atoms.

Compounds of Sulphur.

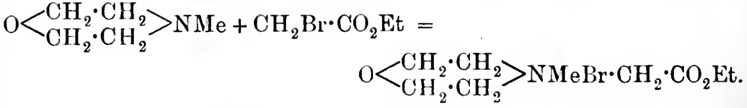
The sulphur analogue of 1:4-dioxan, 1:4-dithian (diethylene disulphide),  $\genfrac{}{}{0pt}{}{CH_2\cdot S\cdot CH_2}{CH_2\cdot S\cdot CH_2}$, also exhibits an augmentation of reactivity when compared with pentamethylene sulphide under as nearly as possible the same conditions. The initial velocity of combination of equimolecular quantities of bromoacetophenone and 1:4-dithian in glacial acetic acid solution at 56·6° is more than three times that of an equimolecular mixture, of the same concentration, of bromoacetophenone and pentamethylene sulphide at the same temperature. The experimental evidence will be discussed more fully later in the paper, when considering the behaviour of 1:4-thioxan.

Compounds containing Nitrogen, with Oxygen or Sulphur.

The cyclic compounds containing a tertiary nitrogen atom were allowed to react under standard conditions with equimolecular quantities of ethyl bromoacetate. Equal volumes of $N/4$-solutions of the base and of ethyl bromoacetate in absolute alcohol were mixed and maintained at 56·6° (corr.), the temperature of the vapour of acetone boiling under 760 mm. pressure. As in the previous investigations, definite portions were withdrawn by means of a pipette standardised for the conditions, and titrated at once by Volhard's method. The reaction is that of normal addition, for example:



$$CH_2{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}{>}NMe + CH_2Br\cdot CO_2Et = CH_2{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}{>}NMeBr\cdot CH_2\cdot CO_2Et.$$



$$O{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}{>}NMe + CH_2Br\cdot CO_2Et = O{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}{>}NMeBr\cdot CH_2\cdot CO_2Et.$$

In the case of the thiazans, there was the possibility of simultaneous addition of the bromoacetic ester to both the nitrogen and the sulphur atoms; that this danger is not present was shown by the isolation of the mono-additive product:

$$S{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}{>}NMeBr\cdot CH_2\cdot CO_2Et$$

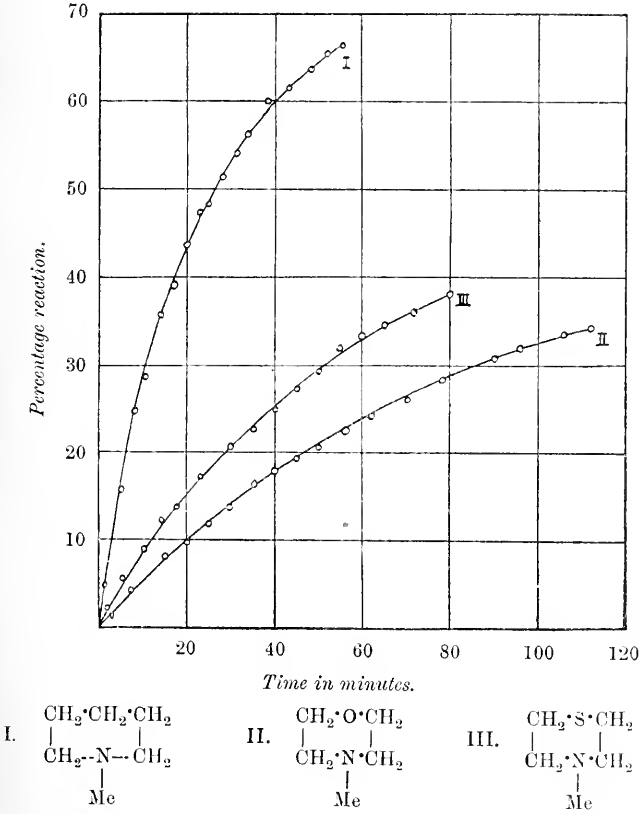
in quantitative yield from the reaction mixture.

The methyl derivatives of the three cyclic systems—piperidine, morpholine, and thiazan—gave the results shown in Fig. 1.

The ethyl derivatives, although all are somewhat more sluggish in reacting, gave qualitatively similar results (Fig 2).

It is thus evident that when the central (γ) methylene group of an alkyl piperidine is replaced by an oxygen atom, the reactive power towards ethyl bromoacetate is considerably diminished. The reactivity of the thiazans, where an atom of sulphur replaces the γ-methylene group, lies between those of the piperidines and the morpholines. On comparing the number of minutes which elapse before a definite proportion of the reaction is completed:

Fig. 1.



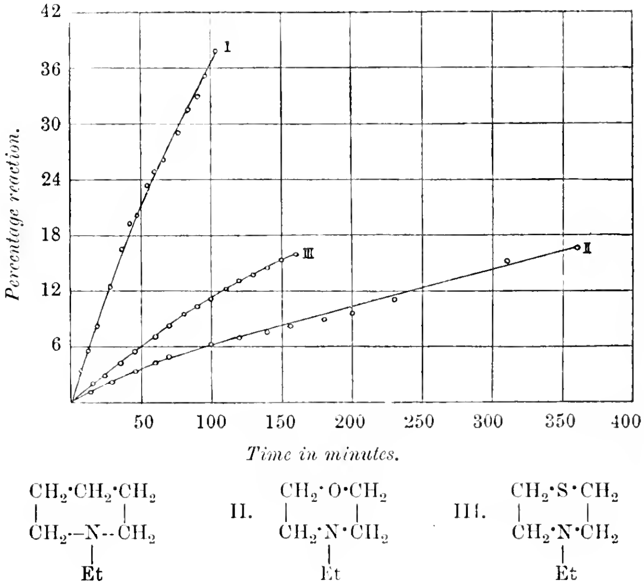
	Time for 10 per cent. reaction.	
	Methyl.	Ethyl.
Piperidine, $\mathrm{CH_2}<\substack{\mathrm{C_2H_4}\\ \mathrm{C_2H_4}}>\mathrm{N{\cdot}R}$	2 minutes	22 minutes
1 : 4-Thiazan, $\mathrm{S}<\substack{\mathrm{C_2H_4}\\ \mathrm{C_2H_4}}>\mathrm{N{\cdot}R}$	11 ,,	87 ,,
Morpholine, $\mathrm{O}<\substack{\mathrm{C_2H_4}\\ \mathrm{C_2H_4}}>\mathrm{N{\cdot}R}$	20 ,,	200 ,,

we find that the ratio of reactivities of the three classes thus expressed is approximately 1 : 5 : 10.

Compounds containing Sulphur, with Oxygen.

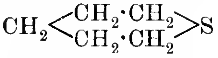
In determining the reactive power of the sulphur atom, equal volumes of $N/2$-solutions of the sulphur compound and bromoacetophenone in glacial acetic acid were mixed and maintained at 56·6°, portions being withdrawn at intervals by means of a standardised pipette and immediately titrated by Volhard's method, the dilute nitric acid being covered by a deep layer of ethyl acetate, which served to remove the excess of bromoacetophenone from the action of the silver nitrate.

FIG. 2.

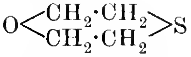


The data, when plotted in the customary manner, show remarkable results. With pentamethylene sulphide a curve was obtained showing a normal rate of addition, in which the reaction proceeds regularly with an easily measurable velocity. 1 : 4-Thioxan, on the other hand, shows an initial velocity of about one-twentieth of this value, and after one hundred and sixty minutes the increase in ionised bromine ceases entirely, the percentage of additive product being 4·5. Subsequent estimations gave precisely the same figure, and even after twenty-one hours' titration of a sample showed the presence of only 4·5 per cent. of sulphonium bromide (Fig. 3).

Here, again, therefore, the replacement of the γ-methylene group in pentamethylene sulphide by an oxygen atom:



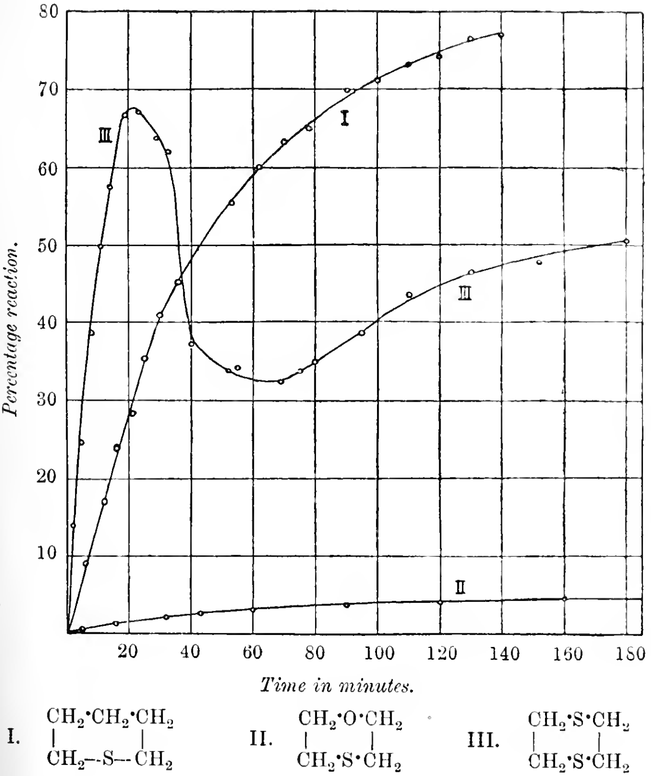
$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>S$$

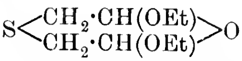


$$O<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>S$$

causes an enormous decrease in the reactive power of the sulphur atom. This is in entire harmony with the observation (Clarke and Smiles, Trans., 1909, **95**, 994) that the sulphur atom in 3:5-diethoxy-1:4-thioxan:

Fig. 3.





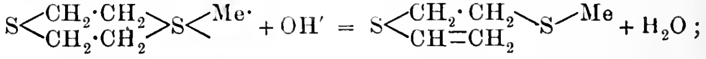
$$S<\begin{matrix}CH_2\cdot CH(OEt)\\CH_2\cdot CH(OEt)\end{matrix}>O$$

is inordinately sluggish in its chemical functions.

Turning now to the reactivity of 1:4-dithian; this was estimated by measuring the rate of conversion of the bromine in bromoacetophenone into a sulphonium bromide in a solution containing equimolecular quantities of the dithian and bromoacetophenone in glacial acetic acid solution, the conditions being exactly the same as with pentamethylene sulphide and thioxan. That this procedure admits of a legitimate comparison is assumed from the observations of Mansfeld (*Ber.*, 1886, **19**, 700), who showed that methyl and ethyl iodides in excess yielded only the monosulphonium derivatives when allowed to react at their boiling points with dithian, and of Strömholm (*Ber.*, 1899, **32**, 2892), who obtained the monothetin of the same substance. Further, Mansfeld showed that the disulphonium derivatives were obtained only by heating dithian with an excess of alkyl iodide to 110—115°. From these facts the author concludes that under the conditions of experiment the initial velocity of sulphonium bromide formation is attributable exclusively to combination with only one of the two sulphur atoms.

The initial velocity thus found was more than three times as great as that with pentamethylene sulphide, a difference so striking as to allow of no doubt that the presence of two atoms of sulphur in the specific position causes increased reactive power.

A most remarkable feature in the curve is that when the proportion of ionised bromine has reached 67 per cent. the reaction appears to cease, this being followed by a rapid, although measureable, decrease in the amount of bromide until the figure reaches 33 per cent., after which the values on titration again begin to rise, although more slowly. This phenomenon can only point to some reaction by which the ionised bromine is absorbed with formation of a new compound containing non-ionised bromine. It is conceivable that some reaction may take place along lines parallel to the spontaneous dehydration of dithian monoalkyl hydroxides, discussed by Mansfeld (*Ber.*, 1886, **19**, 2661) and Victor Meyer (*ibid.*, 3264), which has recently been shown (Green and Sutherland, Trans., 1911, **99**, 1174) to be a reaction of the second order:



$$S<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>S<^{Me\cdot} + OH' = S<\begin{matrix}CH_2\cdot CH_2\\ CH{=}CH_2\end{matrix}\searrow S\nearrow^{Me} + H_2O;$$

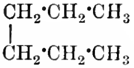
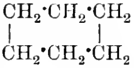
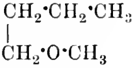
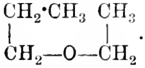
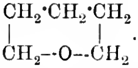
but there is no reason at once apparent why this subsidiary reaction should take place with such precipitation, instead of following the usual rules of mass action. The author hopes to be able further to investigate this problem.

Physical Properties.

Compounds of Oxygen.

Since it was shown (Trans., 1911, **99**, 1927) that the high reactive capacity of the piperazines was accompanied by a small exaltation of refractivity, the refractive power, dispersive power, and molecular volume of a series of compounds have been determined, in order to ascertain whether 1:4-dioxan and the other substances examined possessed anomalous physical properties; and in order to obtain adequate standards of reference, the effect of ring-formation in some substance containing two atoms of ethereal oxygen has been examined.

It may at once be stated that no sort of regularity has been detected between the observed values for molecular dispersion and molecular volume; attention will therefore be principally directed towards the values of molecular refractive power.

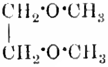
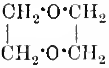
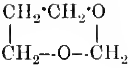
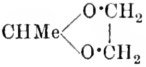
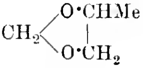
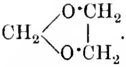
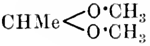
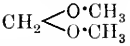
		M_α.	$M_\gamma - M_\alpha$.	Mol. volume at 15°.
* *n*-Hexane,	 $\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH_3 \\ \vert \\ CH_2{\cdot}CH_2{\cdot}CH_3 \end{array}$ ……… …….	29·74	0·720	—
*cyclo*Hexane,	 $\begin{array}{lr} CH_2{\cdot}CH_2{\cdot}CH_2 & \\ \vert \quad\quad \vert & \\ CH_2{\cdot}CH_2{\cdot}CH_2 & \end{array}$ …………..	27·57	0·651	107·39
Methyl *n*-butyl ether,	 $\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH_3 \\ \vert \\ CH_2{\cdot}O{\cdot}CH_3 \end{array}$ …	26·87	0·710	117·69
† Ethyl *n*-propyl ether,	 $\begin{array}{l} CH_2{\cdot}CH_3 \;\; CH_3 \\ \vert \quad\quad\quad \vert \\ CH_2{-}O{-}CH_2 \end{array}$ …	26·82	0·656	—
Pentamethylene oxide,	 $\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH_2 \\ \vert \quad\quad\quad \vert \\ CH_2{-}O{-}CH_2 \end{array}$ …	24·55	0·584	97·12

* Mean of values given by Brühl (*Annalen*, 1880, **200**, 183), and Landolt and Jahn (*Zeitsch. physikal. Chem.*, 1892, **10**, 302).

† Brühl (*loc. cit.*, p. 177).

Accepting the atomic refraction of hydrogen as 1·09, the value of M_α calculated for *cyclo*hexane from *n*-hexane is 27·56, in close agreement with the observed value (27·57). The molecular dispersion $M_\gamma - M_\alpha$ works out to 0·662, as compared with the observed value, 0·651, on deducting twice the atomic dispersion of hydrogen (0·029). The values for atomic refraction and dispersion are those given by Eisenlohr (*Zeitsch. physikal. Chem.*, 1910, **75**, 605). In the analogous compounds in which one of the methylene groups is replaced by an oxygen atom, we find the calculated values of M_α for pentamethylene oxide to be 24·69 and 24·64 when based on the figures for methyl *n*-butyl ether and ethyl *n*-propyl ether respectively, the observed value being 24·55.

On comparing the observed values of M_α and $M_\gamma - M_\alpha$ for *cyclo*hexane and pentamethylene oxide, we find that replacement of a methylene group by an oxygen atom introduces a difference of $-3·02$ units for M_α and $-0·067$ for $M_\gamma - M_\alpha$.

	M_α.	$M_\gamma - M_\alpha$.	Mol. volume at 15°
αβ-Dimethoxyethane,  $\begin{array}{l}CH_2{\cdot}O{\cdot}CH_3\\ \vert\\ CH_2{\cdot}O{\cdot}CH_3\end{array}$	23·72	0·572	103·51
1 : 4-Dioxan, 	21·55	0·500	85·04
1 : 3-Dioxan, 	21·38	0·486	84·63
Ethyleneacetal, 	21·53	0·491	89·16
Propylenemethylal, 	21·63	0· 4	88·54
Ethylenemethylal, 	16·83	0·373	69·41
Dimethylacetal,  $CHMe{<}^{O\cdot CH_3}_{O\cdot CH_3}$	23·66	0·537	105·18
* Dimethylmethylal,  $CH_2{<}^{O\cdot CH_3}_{O\cdot CH_3}$	19·10	0·438	—

* Brühl (*Annalen*, 1880, **203**, 12; *Ber.*, 1897, **30**, 161). Mean of two sets of data.

The calculated values of M_α and $M_\gamma - M_\alpha$ may be derived two ways. Firstly, from the open-chain compound in the ordinary way (method I):

	M_α.	$M_\gamma - M_\alpha$.
αβ-Dimethoxyethane	23·72	0·572
less 2H	−2·18	−0·058
1 : 4-Dioxan (calc.)	21·54	0·514
,, (obs.)	21·55	0·500
Difference	+0·01	−0·014

Secondly, by replacing for a second time a methylene group in the *cyclo*hexane ring by an oxygen atom (method II):

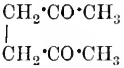
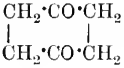
	M_α.	$M_\gamma - M_\alpha$.
*cyclo*Hexane	27·57	0·651
Pentamethylene oxide	24·55	0·584
Replacement of $>CH_2$ by $>O$	−3·02	−0·067
Pentamethylene oxide	24·55	0·584
1 : 4-Dioxan (calc.)	21·53	0·517
,, (obs.)	21·55	0·500
Difference	+0·02	−0·017

Both methods lead to almost identical results—1 : 4-dioxan shows no optical anomaly.

For purposes of comparison, three further cyclic isomerides of

1:4-dioxan were prepared and examined. 1:3-Dioxan (trimethylenemethylal) is a substance closely resembling 1:4-dioxan (except in odour), and shows a very slight optical depression. This substance is noteworthy in that it also exhibits basic properties, which are, however, less pronounced than those of the 1:4-isomeride. Its slightly higher boiling point and greater density are also remarkable, when it is considered that it is a compound of less symmetrical structure. The remaining compounds in the above table call for little comment, beyond the fact that the five-membered rings containing two atoms of oxygen and an external methyl group possess considerably lower densities and boiling points, and show no sign of basic properties. By a comparison of the corresponding open-chain compounds, the physical properties of these five-membered cyclic systems are found to be normal.

To serve as a check, the corresponding carbonyl compounds were also examined, as it has been shown by other considerations (Stewart, "Stereochemistry," 1907, 486) that the conditions obtaining in *cyclo*hexane-1:4-dione are abnormal, owing to mutual influence between the carbonyl groups.

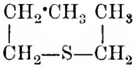
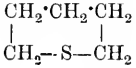
		M_α.	$\gamma - M_\alpha$.
Acetonylacetone,	 $\begin{array}{l} CH_2\cdot CO\cdot CH_3 \\ \vert \\ CH_2\cdot CO\cdot CH_3 \end{array}$ ……………	30·01	0·808
*cyclo*Hexane-1 : 4-dione,	 $\begin{array}{lcr} CH_2\cdot CO\cdot CH_2 \\ \vert & & \vert \\ CH_2\cdot CO\cdot CH_2 \end{array}$ ……	27·79	0·671

From these figures, adopting method of calculation I, *cyclo*hexanedione is found to be optically normal:

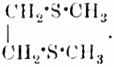
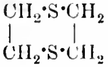
M_α (obs.) 27·79, (calc.) 27·83 ; $M_\gamma - M_\alpha$ (obs.) 0·671, (calc.) 0·750.

Compounds of Sulphur.

Similar measurements were carried out with corresponding sulphur compounds:

		M_α.	$M_\gamma - M_\alpha$.	Mol. volume at 15°.
Ethyl *n*-propyl sulphide,	 $\begin{array}{lcr} CH_2\cdot CH_3 & & CH_3 \\ \vert & & \vert \\ CH_2 - S - CH_2 \end{array}$ …	32·65	0·968	122·50
Pentamethylene sulphide,	 $\begin{array}{lcr} CH_2\cdot CH_2\cdot CH_2 \\ \vert & & \vert \\ CH_2 - S - CH_2 \end{array}$ …	30·61	0·913	103·14

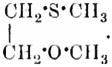
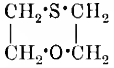
The refractive power of two samples of 1:4-dithian was determined in xylene solution, since it is insufficiently soluble in alcohols.

		M_α
Dimethyl ethylene sulphide,	 $\begin{array}{l}CH_2\cdot S\cdot CH_3\\ \vert\\ CH_2\cdot S\cdot CH_3\end{array}$	36·37
1 : 4-Dithian,	 $\begin{array}{l}CH_2\cdot S\cdot CH_2\\ \vert \qquad\quad \vert\\ CH_2\cdot S\cdot CH_2\end{array}$	32·14

From these data, by method I, 1 : 4-dithian would appear to be optically depressed to the extent of 2·05 units. It is not improbable that in this case the abnormality is due to solvent influence, as a depression of this magnitude is hardly to be expected in such a compound. The question was not considered worthy of further investigation.

Compounds containing Oxygen and Sulphur.

The optical properties of 1 : 4-thioxan were compared with those of the corresponding open-chain compound:

		M_α.	$M_\gamma - M_\alpha$.	Mol. volume at 15°.
Methyl β-methoxyethyl sulphide,	 $\begin{array}{l}CH_2\cdot S\cdot CH_3\\ \vert\\ CH_2\cdot O\cdot CH_3\end{array}$.	29·93	0·895	110·45
1 : 4-Thioxan,	 $\begin{array}{l}CH_2\cdot S\cdot CH_2\\ \vert \qquad\quad \vert\\ CH_2\cdot O\cdot CH_2\end{array}$	27·56	0·812	92·67

The molecular refraction of thioxan calculated from methyl methoxyethyl sulphide by method I appears to be somewhat higher than the observed value:

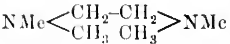
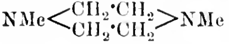
M_α (obs.) 27·56, (calc.) 27·75; $M_\gamma - M_\alpha$ (obs.) 0·812, (calc.) 0·837.

from which we could conclude that thioxan exhibits a slight (0·69 per cent.) optical depression. On the other hand, if we calculate the change in value on replacement of a methylene group in pentamethylene sulphide by an oxygen atom (method II), we obtain a somewhat lower figure, whereby the anomaly all but vanishes:

M_α (obs.) 27·56, (calc.) 27·59; $M_\gamma - M_\alpha$ (obs.) 0·812, (calc.) 0·846.

Compounds of Nitrogen.

In order to make sure that the optical exaltation of the piperazines (Trans., 1911, **99**, 1931) is a phenomenon characteristic of all the members of this series, a comparison was made of dimethylpiperazine and tetramethylethylenediamine:

		M_α.	$M_\gamma - M_\alpha$.	Mol. volume at 15°.
Tetramethylethylenediamine,	 $NMe{<}\begin{array}{l}CH_2{-}CH_2\\ CH_3\quad CH_3\end{array}{>}NMe$	37·39	1·185	148·86
Dimethylpiperazine,	 $NMe{<}\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}{>}NMe$	35·45	1·106	131·95

The values for dimethylpiperazine, observed and calculated by method I, showed the presence of a slight exaltation of refractive power:

M_α (obs.) 35·45, (calc.) 35·21 ; $M_\gamma - M_\alpha$ (obs.) 1·106, (calc.) 1·123.

The difference is not great; nevertheless, it is of the same order as those observed with *iso*amyl and benzyl derivatives when expressed as a percentage of the molecular refraction:

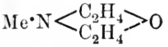
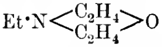
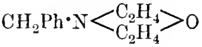
	M_α.	Δ.	Percentage anomaly.
Dimethylpiperazine	35·45	+0·24	+0·68
Di*iso*amylpiperazine	72·46	+0·52	+0·72
Dibenzylpiperazine	83·83	+0·49	+0·59

For the calculation of the morpholines and the thiazans, the corresponding derivatives of piperidine were selected, as in the reactivity measurements, as standards:

	M_α.	$M_\gamma - M_\alpha$.	Mol. volume at 15°.
Methylpiperidine, $Me\cdot NC_5H_{10}$	31·69	0·922	120·80
Ethylpiperidine, $Et\cdot NC_5H_{10}$	36·27	1·044	136·51
Benzylpiperidine, $CH_2Ph\cdot NC_5H_{10}$	55·63	2·116	181·44

Compounds containing Nitrogen and Oxygen.

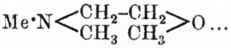
The three derivatives of morpholine gave the following figures:

	M_α.	$M_\gamma - M_\alpha$.	Mol. volume at 15°.
Methylmorpholine,  $Me\cdot N<\substack{C_2H_4\\C_2H_4}>O$	28·59	0·804	109·62
Ethylmorpholine,  $Et\cdot N<\substack{C_2H_4\\C_2H_4}>O$	33·32	0·764	125·47
Benzylmorpholine,  $CH_2Ph\cdot N<\substack{C_2H_4\\C_2H_4}>O$ ...	52·52	1·971	170·40

Calculated values for these substances can be obtained by method II from the figures observed for the piperidines:

	Methyl-morpholine.	Ethyl-morpholine.	Benzyl-morpholine.
M_α	28·67	33·25	52·61
$M_\gamma - M_\alpha$	0·855	0·977	2·049

The open-chain compounds corresponding with methylmorpholine and benzylmorpholine, namely, methyl dimethylaminoethyl ether, and methyl benzylmethylaminoethyl ether, were also examined:

		M_α.	$M_\gamma - M_\alpha$.	Mol. volume at 15°
Methyl dimethylamino-ethyl ether,	 $Me\cdot N<\substack{CH_2-CH_2\\CH_3\ \ CH_3}>O$ ...	30·71	0·974	126·55
Methyl benzylmethyl-aminoethyl ether,	 $CH_2Ph\cdot N<\substack{CH_2-CH_2\\CH_3\ \ CH_3}>O$	54·89	2·078	186·89

From these the calculated values for methylmorpholine and benzylmorpholine can be derived, adopting method I:

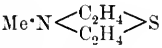
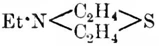
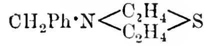
Methylmorpholine: M_α (obs.) 28·59, (calc.) 28·53; $M_\gamma - M_\alpha$ (obs.) 0·804, (calc.) 0·916
Benzylmorpholine: ,, 52·52, ,, 52·71; ,, 1·971, ,, 2·020

These results point to the absence of any pronounced type of optical anomaly in the three derivatives of morpholine examined. That the present author had grounds for anticipating the reverse will be understood on reference to a paper of Knorr (*Annalen*, 1898, **301**, 11, 15), in which the figures given for both methylmorpholine and ethylmorpholine show distinct optical exaltation for the sodium *D*-line.

Compounds containing Nitrogen and Sulphur.

The details of the members of the thiazan series here referred to have already been communicated (this vol., p. 1583).

The molecular physical constants are as follows:

	M_α.	$M_\gamma - M_\alpha$.	Mol. volume at 15°.
Methylthiazan,  $\mathrm{Me{\cdot}N}{<}\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}{>}S$	34·78	1·168	117·47
Ethylthiazan,  $\mathrm{Et{\cdot}N}{<}\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}{>}S$	39·09	1·234	131·93
Benzylthiazan,  $\mathrm{CH_2Ph{\cdot}N}{<}\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}{>}S$...	58·36	3·128	176·12

The calculated values can, like those of the morpholines, be deduced from the figures of the piperidines, by introducing the numbers derived by the replacement of methylene by sulphur:

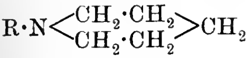
	M_α.	$M_\gamma - M_\alpha$.
*cyclo*Hexane........................	27·57	0·651
Pentamethylene sulphide	30·61	0·913
Replacement of $>CH_2$ by $>S$	+3·04	+0·262

	Methylthiazan.	Ethylthiazan.	Benzylthiazan.
M_α..................	34·73	39·31	58·67
$M_\gamma - M_\alpha$	1·184	1·306	2·378

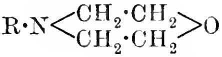
As in the morpholines, there is no decisive regularity of anomaly throughout the series. The enormous exaltation of dispersive power of benzylthiazan is worthy of notice.

Discussion of Results.

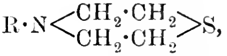
There can be little doubt that in the comparison of the initial rates of addition of halogen compounds to the cyclic systems above described, the reactivity is a true index of the amount of residual affinity of the atoms the valencies of which are thus raised by the addition. In the series



$$\mathrm{R\cdot N}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH_2}$$



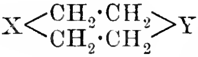
$$\mathrm{R\cdot N}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{O}$$



$$\mathrm{R\cdot N}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{S},$$

where the alkyl groups R are identical, there is no reason to assume that the replacement of the γ-methylene group in piperidine by an atom of oxygen or of sulphur should introduce any profound stereochemical alteration; whilst the increase in molecular weight, due, for instance, to the transition from methylpiperidine to methylmorpholine, is scarcely sufficient to account for so great a difference in reactivity.

The chemical evidence here collected, and taken in conjunction with that described in Part II, leads to the following definite conclusions:



(1) That in cyclic compounds of the type $\mathrm{X}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{Y}$, the two atoms represented by X and Y—which are capable of raising their valency, and to which residual affinity is attributable—influence each other in such a way as to affect their reactive power.

(2) That when the atoms X and Y are atoms of the same element (either two oxygen, two nitrogen, or two sulphur atoms), the effect of the mutual influence is to increase the reactivity.

(3) That when the atoms X and Y are atoms of different elements (either oxygen and nitrogen, oxygen and sulphur, or nitrogen and sulphur), the reactivity is decreased.

It would be premature to base any theory touching the nature of residual affinity of such atoms on these facts; more material must be collected by a study of other properties besides reactive power. The physical properties above detailed are apparently incapable of detecting such influences with certainty; refractive power would seem to be insufficiently sensitive, whilst the variations of molecular dispersion and molecular volume are so indefinite that they permit of the formation of no general conclusions. It is not unlikely, however, that a study of the absorption spectra, molecular heats of combustion, and compressibility of these compounds would lead to serviceable results.

EXPERIMENTAL.

cyclo*Hexane*.—Purified by fractional distillation over sodium. B. p. 81·0°/768 mm.:

$$D^{15^\circ}_{4^\circ}\ 0{\cdot}78220,\quad D^{20^\circ}_{4^\circ}\ 0{\cdot}77805,\quad n^{20^\circ}_{\alpha}\ 1{\cdot}42438,\quad n^{20^\circ}_{\gamma}\ 1{\cdot}43588.$$

Methyl n-*Butyl Ether*.—Sodium was added in small quantities to pure *n*-butyl alcohol until the sodium *n*-butyloxide began to separate. Methyl iodide corresponding with the amount of sodium present was then added, and the mixture heated for three hours on the water-bath under reflux. On distillation, the fraction b. p. 70—80° was collected and repeatedly boiled with sodium until no further action took place. The pure ether was obtained as a liquid boiling at 71°/760 mm., possessing the properties ascribed to it by Henry (*Bull. Soc. chim.*, 1891, [iii], **7**, 151), who prepared it by a different method:

$$D_{4^\circ}^{15^\circ}\ 0{\cdot}74773,\ D_{4^\circ}^{20^\circ}\ 0{\cdot}74433,\ n_{\alpha}^{20^\circ}\ 1{\cdot}37202,\ n_{\gamma}^{20^\circ}\ 1{\cdot}38306.$$

Pentamethylene Oxide.—Twenty-five grams of αε-dibromopentane, prepared and purified by v. Braun's method (*Ber.*, 1904, **37**, 3210; 1905, **38**, 2339), were mixed with 25 grams of water and 8 grams of pure zinc oxide; the mixture was well shaken, so as to form an emulsion, and heated in a sealed tube for forty hours at 150°. The zinc oxide had then almost disappeared. The resulting mixture was distilled in a current of steam, and the oil separated from the distillate. After drying with solid potassium hydroxide and sodium, it distilled constantly at 88°/760 mm. Hochstetter (*Monatsh.*, 1902, **23**, 1073), who prepared it by heating the possibly impure dibromopentane, prepared from cadaverine, with twenty volumes of water to 100° for a fortnight, gives the boiling point as 81—82°. It is a colourless liquid of characteristic and agreeable odour, almost insoluble in water. The yield was almost quantitative:

$$D_{4^\circ}^{15^\circ}\ 0{\cdot}88550,\ D_{4^\circ}^{20^\circ}\ 0{\cdot}88135,\ n_{\alpha}^{20^\circ}\ 1{\cdot}41722,\ n_{\gamma}^{20^\circ}\ 1{\cdot}42857.$$

αβ-Dimethoxyethane.—The disodium derivative of ethylene glycol was prepared according to the directions of Lippert (*Annalen*, 1893, **276**, 171) from 21 grams of glycol and 15 grams of sodium in ethyl alcohol, and mixed with 82 grams (2 mols.) of methyl sulphate. The mixture was heated in a distilling flask on the oil-bath. At 90° a violent reaction set in; a liquid distilled over, and a large quantity of black residue remained in the flask. The distillate was boiled with solid potassium hydroxide, and the clear liquid separated and distilled. The fraction boiling up to 90° was repeatedly boiled with metallic sodium until no further reaction took place, filtered, and distilled over sodium. The pure substance was obtained as a colourless liquid boiling at 78°/750 mm., miscible with water, and possessing a rather sharp ethereal odour. The yield was poor. Lippert, who prepared this ether by heating the disodium salt of ethylene glycol with methyl iodide for over a week, states that it boils at 82—83°/713 mm., but it is questionable whether his product was pure, as his determination of its vapour density was distinctly too low. This ether yields no precipitate with aqueous mercuric chloride, and does not react with bromine at 0° or at 20°:

$$D_{4°}^{15°}\ 0{\cdot}86877,\ D_{4°}^{20°}\ 0{\cdot}86285,\ n_{\alpha}^{20°}\ 1{\cdot}37216,\ n_{\gamma}^{20°}\ 1{\cdot}38224.$$

1:4-*Dioxan* (*Diethylene Dioxide*).—Prepared according to the directions of Faworsky (*loc. cit.*), by heating a 4 per cent. solution of concentrated sulphuric acid in ethylene glycol on the oil-bath. The distillate was saturated with potassium hydroxide, and the separated liquid distilled over sodium. It is a colourless liquid, miscible with water, boiling at 101°/750 mm.:

$$D_{4°}^{15°}\ 1{\cdot}03484,\ D_{4°}^{20°}\ 1{\cdot}03034,\ n_{\alpha}^{20°}\ 1{\cdot}41848,\ n_{\gamma}^{20°}\ 1{\cdot}42961.$$

The mercurichloride, described by Paternò and Spallinò (*loc. cit.*), is stable, and sublimes unchanged on heating.

The acetals described below are all prepared by the following method. The glycol was heated in a sealed tube with a little more than the calculated amount of polyoxymethylene ("trioxymethylene") or aldehyde and the same quantity of pure orthophosphoric acid for about twenty-four hours at 100°. The mixture was rendered faintly alkaline with dilute sodium hydroxide and distilled. The distillate was saturated with solid potassium hydroxide, and the separated liquid dried by boiling with solid potassium hydroxide and subsequently distilled over sodium. The yields were in every case excellent.

1:3-*Dioxan* (*Trimethylenemethylal*).—From 10 grams of trimethylene glycol, 5 grams of polyoxymethylene, and 5 grams of orthophosphoric acid. Yield: 10 grams of crude, dry product. It is a colourless liquid of agreeable acetal-like odour, miscible with water, and boiling at 105°/755 mm. Henry (*Bull. Acad. roy. Belg.*, 1902, 460) gives the boiling point as 106°:

$$D_{4°}^{15°}\ 1{\cdot}03987,\ D_{4°}^{20}\ 1{\cdot}03422,\ n_{\alpha}^{20°}\ 1{\cdot}41652,\ n_{\gamma}^{20°}\ 1{\cdot}42730.$$

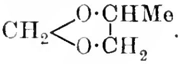
The *mercurichloride* is obtained as a white precipitate from cold aqueous solution; it is soluble in hot water, from which it crystallises in needles on cooling. It sinters and decomposes at about 126°, but otherwise closely resembles the mercurichloride of 1:4-dioxan.

A pale yellow, crystalline *picrate*, melting indistinctly at 57°, is formed when a solution of picric acid in 1:3-dioxan is rapidly evaporated at 0° under diminished pressure in a current of air. This compound rapidly loses dioxan, and after remaining in air on a porous tile for eighteen hours is completely reconverted into picric acid melting sharply at 121°.

Owing to its acetal grouping, 1:3-dioxan is immediately decomposed by bromine at 0°, with formation of a heavy oil insoluble in water, but gradually decomposed thereby.

Ethyleneacetal.—Prepared from ethylene glycol, acetaldehyde, and orthophosphoric acid. It boils at 83—84°/755 mm., and is miscible with water. It gives no precipitate with mercuric chloride:

$D_{4^\circ}^{15^\circ}$ 0·98703, $D_{4^\circ}^{20^\circ}$ 0·98112, $n_{\alpha}^{20^\circ}$ 1·39553, $n_{\gamma}^{20^\circ}$ 1·40576.

Propylenemethylal, 
$CH_2\!<\!\begin{matrix}O\cdot CHMe\\ |\\ O\cdot CH_2\end{matrix}$.—This compound is not described in the literature. It was prepared from propylene glycol, polyoxymethylene, and orthophosphoric acid. It boils at 88—89°/755 mm., and is soluble in about ten parts of cold water:

0·1254 gave 0·2505 CO_2 and 0·1058 H_2O. C = 54·5; H = 9·4.
$C_4H_8O_2$ requires C = 54·5; H = 9·1 per cent.

$D_{4^\circ}^{15^\circ}$ 0·99385, $D_{4^\circ}^{20^\circ}$ 0·98855, $n_{\alpha}^{20^\circ}$ 1·40109, $n_{\gamma}^{20^\circ}$ 1·41107.

Ethylenemethylal.—Prepared from ethylene glycol, polyoxymethylene, and orthophosphoric acid. It boils at 76°/755 mm., and is miscible with water:

$D_{4^\circ}^{15^\circ}$ 1·06617, $D_{4^\circ}^{20^\circ}$ 1·06001, $n_{\alpha}^{20^\circ}$ 1·39736, $n_{\gamma}^{20^\circ}$ 1·40734.

Dimethylacetal.—This was fractionally distilled over sodium. It boils at 64°/748 mm.:

$D_{4^\circ}^{15^\circ}$ 0·85568, $D_{4^\circ}^{20^\circ}$ 0·85015, $n_{\alpha}^{20^\circ}$ 1·36506, n^{20° 1·37433.

Acetonylacetone.—After redistillation the fraction boiling at 192—194° was examined:

$D_{4^\circ}^{15^\circ}$ 0·97794, $D_{4^\circ}^{20^\circ}$ 0·97370, $n_{\alpha}^{20^\circ}$ 1·42625, $n_{\gamma}^{20^\circ}$ 1·43944.

cyclo*Hexane*-1 : 4-*dione.*—After recrystallisation from a mixture of alcohol and light petroleum the substance had the correct melting point, 78°.

I. *In Alcohol.*

Solvent: $D^{16\cdot8^\circ}$ 0·79252, $n_{\alpha}^{16\cdot8^\circ}$ 1·36097, $n_{\gamma}^{16\cdot8^\circ}$ 1·37059; weight 3·8894.
Solution: $D^{17\cdot4^\circ}$ 0·81466, $n_{\alpha}^{17\cdot4^\circ}$ 1·36853, $n_{\gamma}^{17\cdot4^\circ}$ 1·37841; weight 4·2310.
Whence $M_{\alpha} = 27\cdot80$, $M_{\gamma} - M_{\alpha} = 0\cdot690$.

II. *In Alcohol.*

Solvent: $D^{16\cdot8^\circ}$ 0·79252, $n_{\alpha}^{16\cdot8^\circ}$ 1·36097, $n_{\gamma}^{16\cdot8^\circ}$ 1·37059; weight 2·2792.
Solution: $D^{17\cdot5^\circ}$ 0·81303, $n_{\alpha}^{17\cdot5^\circ}$ 1·36792, $n_{\gamma}^{17\cdot5^\circ}$ 1·37771; weight 2·4652.
Whence $M_{\alpha} = 27\cdot78$, $M_{\gamma} - M_{\alpha} = 0\cdot652$.

Ethyl n-*Propyl Sulphide.*—This was prepared by the action of *n*-propyl bromide on an alcoholic solution of the sodium salt of ethyl mercaptan (Strömholm, *Ber.*, 1900, **33**, 830). The reaction mixture was distilled in a current of steam, and an excess of dilute mercuric chloride added to the distillate. The mercurichloride was precipitated as a heavy oil, which was washed with concentrated calcium chloride solution (to remove traces of alcohol) and with water, and decomposed by distillation with aqueous sodium sulphide. The oily sulphide was dried with solid potassium hydroxide, and repeatedly fractionally distilled over metallic sodium. A fraction boiling at 115—117° was collected for examination:

$$D_{4^\circ}^{15^\circ}\ 0{\cdot}84901,\ D_{4^\circ}^{20^\circ}\ 0{\cdot}84448,\ n_{\alpha}^{20^\circ}\ 1{\cdot}44305,\ n_{\gamma}^{20^\circ}\ 1{\cdot}45827.$$

Pentamethylene Sulphide.—Prepared by the interaction of αε-dichloropentane and alcoholic potassium sulphide.

The dichloropentane was prepared by v. Braun's method (*Ber.*, 1904, **37**, 2918). It was found that the most convenient method of removing the benzonitrile from the mixture was to shake it repeatedly with cold concentrated sulphuric acid until no further colour was imparted to the acid. The pure dichloropentane then boiled, after washing with water and drying with calcium chloride, in its entirety and without any decomposition between 179·5° and 180·5°. It may here be observed that αε-dibromopentane cannot thus be purified, as it does not readily form a separate layer over sulphuric acid, and is, moreover, slightly decomposed by this reagent, even in the cold.

Fifteen grams of αε-dichloropentane were warmed with a dilute alcoholic solution of twice the calculated quantity of potassium sulphide on the water-bath for two hours under reflux. The mixture was distilled in a current of steam, excess of dilute mercuric chloride added to the distillate, and the crystalline mercurichloride collected and well washed with water. This was decomposed by distillation with aqueous sodium sulphide, and the oil separated from the distillate. After drying by boiling with solid potassium hydroxide and with sodium, the entire quantity passed over at 141°/755 mm. (v. Braun, *Wallach-Festschrift*, 1909, 381, gives 140—142°). The substance is a colourless liquid of unpleasant odour, insoluble in water, and miscible with organic liquids. Below 13° it completely solidifies to a crystalline mass, melting at 13°:

$$D_{4^\circ}^{15^\circ}\ 0{\cdot}98892,\ D_{4^\circ}^{20^\circ}\ 0{\cdot}98489,\ n_{\alpha}^{20^\circ}\ 1{\cdot}50295,\ n_{\gamma}^{20^\circ}\ 1{\cdot}52223.$$

Dimethyl Ethylene Sulphide.—This was prepared from ethylene bromide and the sodium salt of methyl mercaptan in alcohol. It boils at 183°:

$$D_{4^\circ}^{15^\circ}\ 1{\cdot}04189,\ D_{4^\circ}^{20^\circ}\ 1{\cdot}03660,\ n_{\alpha}^{20^\circ}\ 1{\cdot}53026.$$

1:4-*Dithian.*—This was prepared by the usual method. It melted sharply at 111°. This substance is insufficiently soluble in alcohol to determine the refractive power in this solvent.

I. *In Xylene.*

Solvent: D$^{22\cdot8^\circ}$ 0·85744, $n_\alpha^{22\cdot8^\circ}$ 1·48790; weight 2·6298.
Solution: D$^{23\cdot0^\circ}$ 0·87719, $n_\alpha^{23\cdot0^\circ}$ 1·49265; weight 2·8720.
Whence $M_\alpha = 32\cdot13$.

II. *In Xylene.*

Solvent: D$^{22\cdot8^\circ}$ 0·85744, $n_\alpha^{22\cdot8^\circ}$ 1·48790; weight 2·0340.
Solution: D$^{23\cdot2^\circ}$ 0·87732, $n_\alpha^{23\cdot2^\circ}$ 1·49270; weight 2·2223.
Whence $M_\alpha = 32\cdot14$.

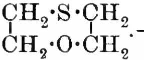
Methyl β-Methoxyethyl Sulphide, $MeO\cdot CH_2\cdot CH_2\cdot SMe$.—This compound is not described in the literature. It was prepared by the interaction of methyl β-iodoethyl ether, $MeO\cdot CH_2\cdot CH_2I$, and sodium methyl mercaptide.

The methyl iodoethyl ether was prepared by a modification of Karvonen's method (*Ber.*, 1909, **42**, 690). A mixture of 35 grams of finely powdered potassium iodide, 24 grams of methyl alcohol, and 19 grams of ethylene dibromide was heated in a sealed tube for fifteen minutes in steam, and then for forty hours on the water-bath. The product was worked up according to Karvonen's directions. The yield obtained was as good as by the original method.

A mixture of 30 grams of methyl iodoethyl ether, 10 grams of methyl mercaptan, and a solution of 4 grams of sodium in 40 c.c. of methyl alcohol was heated at 60° in a sealed tube for twenty hours. The mixture was rendered alkaline, distilled in a current of steam, and the product purified, like pentamethylene sulphide, through the mercurichloride. It is a colourless, mobile liquid, sparingly soluble in water, possessing a characteristic, mustard-like odour. It boils at 131°/755 mm.:

0·1307 gave 0·2144 CO_2 and 0·1144 H_2O. C=44·8; H=9·7.
$C_4H_{10}OS$ requires C=45·3; H=9·4 per cent.
D$^{15^\circ}_{4^\circ}$ 0·95973, D$^{20^\circ}_{4^\circ}$ 0·95508, $n_\alpha^{20^\circ}$ 1·45178, $n_\gamma^{20^\circ}$ 1·46749.

The *mercurichloride* crystallises from alcohol in needles which melt at 74°.

1:4-*Thioxan,*  $\begin{matrix} CH_2\cdot S\cdot CH_2 \\ | \qquad\quad | \\ CH_2\cdot O\cdot CH_2 \end{matrix}$.—This compound is not described in the literature. Thirty grams of ββ′-di-iodoethyl ether, prepared according to the directions of Sand (*Ber.*, 1900, **33**, 1352; 1901, **34**, 1391, 2906), with twice the calculated quantity of dilute alcoholic potassium sulphide, were warmed for two hours—with occasional shaking, as the ether is insoluble in alcohol—on the water-bath under reflux. The product was worked up in the same manner as pentamethylene sulphide, through the mercurichloride. The entire quantity boiled constantly at 147°/755 mm. It is a colourless liquid, sparingly soluble in water, but miscible with extremely dilute aqueous alcohol. The odour recalls those of both 1:4-dioxan and 1:4-dithian, and is far less sharp than that of methyl β-methoxyethyl sulphide:

0·1450 gave 0·2446 CO_2 and 0·1081 H_2O. C=46·0; H=8·3.
C_4H_8OS requires C=46·2; H=7·7 per cent.

$D^{15^\circ}_{4^\circ}$ 1·12229, $D^{20^\circ}_{4^\circ}$ 1·11775, $n^{20^\circ}_{\alpha}$ 1·50429, $n^{20^\circ}_{\gamma}$ 1·52223.

The *mercurichloride* crystallises from alcohol in silky needles melting at 171°.

Tetramethylethylenediamine.—This was prepared by the interaction of ethylene dibromide (1 mol.) and dimethylamine (4 mols.) in alcohol. It boiled constantly at 121°/760 mm. (Knorr, *Ber.*, 1904, **37**, 3510, gives 120—122°):

$D^{15^\circ}_{4^\circ}$ 0·78107, $D^{20^\circ}_{4^\circ}$ 0·77654, $n^{20^\circ}_{\alpha}$ 1·41480, $n^{20^\circ}_{\gamma}$ 1·42984.

Dimethylpiperazine.—Prepared from piperazine and sodium methyl sulphate. It boiled at 131—132°/764 mm., agreeing with the boiling point stated by Knorr, Hörlein, and Roth (*Ber.*, 1895, **28**, 3137):

$D^{15^\circ}_{4^\circ}$ 0·86398, $D^{20^\circ}_{4^\circ}$ 0·85996, $n^{20^\circ}_{\alpha}$ 1·44738, $n^{20^\circ}_{\gamma}$ 1·46359.

Methylpiperidine.—This was obtained by warming a mixture of methyl iodide (1 mol.), piperidine ($1\frac{1}{4}$ mols.), and potassium hydroxide ($1\frac{1}{4}$ mols.) in alcohol for two hours on the water-bath under reflux. The excess of piperidine was removed by shaking the basic products with benzoyl chloride and dilute alkali, faintly acidifying the mixture with acetic acid, and extracting the benzoylpiperidine with ether. On distillation over sodium it boiled at 107°/760 mm.:

$D^{15^\circ}_{4^\circ}$ 0·81957, $D^{20^\circ}_{4^\circ}$ 0·81592, $n^{20^\circ}_{\alpha}$ 1·43549, $n^{20^\circ}_{\gamma}$ 1·45012.

Ethylpiperidine.—Prepared from ethyl iodide and piperidine in the manner described for methylpiperidine. It boiled at 129°/760 mm.:

$D^{15^\circ}_{4^\circ}$ 0·82775, $D^{20^\circ}_{4^\circ}$ 0·82373, $n^{20^\circ}_{\alpha}$ 1·44158, $n^{20^\circ}_{\gamma}$ 1·45629.

Benzylpiperidine.—Prepared from benzyl chloride and piperidine. The product was fractionated under diminished pressure, and boiled at 119°/13 mm.:

$D^{15^\circ}_{4^\circ}$ 0·96451, $D^{20^\circ}_{4^\circ}$ 0·96049, n^{20}_{α} 1·52269, $n^{20^\circ}_{\gamma}$ 1·54661.

The morpholines were prepared by the interaction of one molecular proportion of $\beta\beta'$-di-iodoethyl ether and two molecular proportions of primary alkylamine in alcoholic solution, in presence of sodium acetate or potassium hydroxide. It is noteworthy that the di-iodo-ether, which is insoluble in absolute alcohol, readily dissolves in an alcoholic solution of an aliphatic amine. By this method the morpholine derivatives were obtained in 50 to 60 per cent. yield, and were identified by their picrates.

Methylmorpholine.—A mixture of 20 grams of $\beta\beta'$-di-iodoethyl ether, 11 grams of 33 per cent. alcoholic methylamine, 22 grams of 33 per cent. aqueous potassium hydroxide, and about 20 c.c. of alcohol, was shaken in steam for four hours. The base was separated from a concentrated aqueous solution (prepared by distillation in a current of steam) by saturating with potassium hydroxide, and was freed from moisture and methylamine by boiling under reflux with solid potassium hydroxide. It was finally distilled over sodium, and boiled at 116—117°/764 mm.:

$$D_{4^\circ}^{15^\circ}\ 0{\cdot}92136,\ D_{4^\circ}^{20^\circ}\ 0{\cdot}91683,\ n_{\alpha}^{20^\circ}\ 1{\cdot}43226,\ n_{\gamma}^{20^\circ}\ 1{\cdot}44627.$$

Ethylmorpholine.—Prepared in a similar manner from a mixture of 20 grams of $\beta\beta'$-di-iodoethyl ether, 18 grams of 33 per cent. alcoholic ethylamine, and 22 grams of 33 per cent. potassium hydroxide, with about 20 c.c. of alcohol. It boiled at 138—139°/763 mm.:

$$D_{4^\circ}^{15^\circ}\ 0{\cdot}91657,\ D_{4^\circ}^{20^\circ}\ 0{\cdot}91154,\ n_{\alpha}^{20^\circ}\ 1{\cdot}43881,\ n_{\gamma}^{20^\circ}\ 1{\cdot}45283.$$

Benzylmorpholine.—A mixture of 22 grams (1 mol.) of $\beta\beta'$-di-iodoethyl ether, 10 grams ($1\frac{1}{4}$ mol.) of benzylamine, 12 grams (2 mols.) of sodium acetate, and an excess of anhydrous potassium carbonate was heated in alcoholic solution for four hours on the water-bath under reflux. The alcohol was distilled off, and the residue acidified with dilute sulphuric acid and shaken with ether to remove impurities. The solution was then rendered alkaline, and the basic oil extracted with ether. The ethereal solution was dried with solid potassium hydroxide and submitted to distillation, finally under diminished pressure. The benzylmorpholine, which passed over at 128—129°/13 mm., showed the correct boiling point (about 260°) under atmospheric pressure. It is a colourless oil, closely resembling benzylpiperidine:

$$D_{4^\circ}^{15^\circ}\ 1{\cdot}03396,\ D_{4^\circ}^{20^\circ}\ 1{\cdot}03874,\ n_{\alpha}^{20^\circ}\ 1{\cdot}52565,\ n_{\gamma}^{20^\circ}\ 1{\cdot}54942.$$

Methyl Dimethylaminoethyl Ether, $N(Me)_2{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$.—6·3 Grams (1 mol.) of methyl β-iodoethyl ether, 10 grams (rather more than 2 mols.) of 33 per cent. alcoholic dimethylamine, and 3 c.c. of alcohol were heated in a sealed tube on the water-bath for fifteen hours. The product was worked up in the manner described for methylmorpholine. It is a colourless liquid with an extremely powerful ammoniacal odour, and strongly basic. It boiled constantly at 101°/757 mm.:

0·1124 gave 0·2388 CO_2 and 0·1344 H_2O. C=57·9; H=13·3.

$C_5H_{13}ON$ requires C=58·2; H=12·6 per cent.

$$D_{4^\circ}^{15^\circ}\ 0{\cdot}81391,\ D_{4^\circ}^{20^\circ}\ 0{\cdot}80988,\ n_{\alpha}^{20^\circ}\ 1{\cdot}95483,\ n_{\gamma}^{20^\circ}\ 1{\cdot}99517.$$

The *picrate* is extremely soluble in alcohol, and is precipitated therefrom as a yellow oil on addition of light petroleum.

Methyl Benzylmethylaminoethyl Ether,

$$CH_2Ph\cdot NMe\cdot CH_2\cdot CH_2\cdot OMe.$$

—5·4 Grams (1 mol.) of β-iodoethyl ether, 7·0 grams (2 mols.) of benzylmethylamine, and about 10 c.c. of alcohol were heated in a sealed tube at 100° for twenty-two hours. The product was worked up exactly as described for benzylmorpholine, and the fraction boiling at 117—121°/15 mm. collected and again distilled under diminished pressure. The pure product then boiled constantly at 116°/14 mm. It is a colourless liquid, almost odourless, closely resembling benzylpiperidine:

0·1059 gave 0·2856 CO_2 and 0·0937 H_2O. C = 73·6; H = 9·8.

$C_{11}H_{17}ON$ requires C = 73·8; H = 9·5 per cent.

$D^{15°}_{4°}$ 0·95772, $D^{20°}_{4°}$ 0·95382, $n^{20°}_{\alpha}$ 1·49672, $n^{20°}_{\gamma}$ 1·51907.

The *picrate* is very soluble in alcohol, and is precipitated as an oil by light petroleum.

The experimental details concerning the thiazans have already been described (this vol., p. 1583), and in this connexion there only remains to be added an account of the interaction of ethyl bromoacetate and 4-methyl-1:4-thiazan. On allowing a solution of methylthiazan in the calculated quantity of *N*/4-alcoholic ethyl bromoacetate to remain at the room temperature, after about twelve hours a white, crystalline precipitate appears on disturbing the liquid. After twenty-four hours the reaction is complete. This precipitate, which is only sparingly soluble in cold alcohol, somewhat more so in warm alcohol, and extremely soluble in water, may be recrystallised from 90 per cent. alcohol, and consists in all probability of *ethyl 4-bromo-4-methyl-1:4-thiazan-4-acetate*,

$$S\langle\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\rangle NMeBr\cdot CH_2\cdot CO_2Et:$$

0·3820 required 26·8 c.c. of *N*/20-$AgNO_3$. Br = 28·1.

$C_9H_{18}O_2NBrS$ requires Br = 28·2 per cent.

It sinters, with vigorous evolution of gas, at 219° (uncorr.), leaving a white, infusible residue, which gradually becomes brown at about 300°.

The same product was obtained in a pure state on evaporating to dryness the alcoholic solution after completion of the reaction at 56·6° under the conditions obtaining in the reaction-velocity experiments.

The author desires to express his gratitude to Professor Emil Fischer for the facilities afforded to him in his laboratory.

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CXCII.—*The Absorption Spectra of Simple Aliphatic Substances in Solutions, Vapours, and Thin Films. Part I. Saturated Aldehydes and Ketones.*

By JOHN EDWARD PURVIS and NIAL PATRICK McCLELAND.

IN a recent paper on the absorption spectra of some substances containing two benzene nuclei (this vol., p. 1514), the authors draw some conclusions as to the mutual effect on one another of two oscillation centres in a molecule. In order to study this point further, it was decided to investigate substances of a simple nature containing one oscillating centre, or two similar centres, so as to obtain evidence which might make it possible to build up the absorption spectrum of a substance from the known types of oscillation of the various oscillation centres composing it.

The aim of this paper is to describe the results obtained from a comparative study of various aliphatic aldehydes and ketones in order to determine in what direction, and how far, their absorption of light is affected when such substances are in solution, as vapours and in thin films. The substances examined were: Formaldehyde, acetaldehyde, propionaldehyde, chloral, chloral hydrate, glyoxal, acetone, chloroacetone, methyl ethyl ketone, diethyl ketone, acetylacetone, and diacetyl. The experimental methods have been described before. The sources of light were the cadmium spark; the uranium-molybdenum spark; the copper spark; also an acetylene flame was used in the investigation of the least refrangible absorption bands of the vapours of glyoxal and diacetyl. Stewart and Baly (Trans., 1906, **89**, 492) have studied solutions of various methyl ketones, two of which observations have been repeated by the authors to compare with the vapours.

Solutions.

Formaldehyde.—Efforts were made to obtain solutions of the substance in alcohol and in ether by passing the vapour into the solvent. It was found that it rapidly polymerised in ether, and there was no selective absorption; in alcohol it appeared gradually to combine with the solvent, and anomalous results were obtained. There was, however, a considerable amount of general absorption; for, through a thickness of 90 mm. the rays were absorbed in an ethereal solution from about λ 2680. In another *N*/2-alcoholic solution, the rays were absorbed from about λ 2800 through a thickness of 38 mm.

Acetaldehyde.—A normal alcoholic solution showed a band at about 1/λ 3500 (Fig. 1, II).

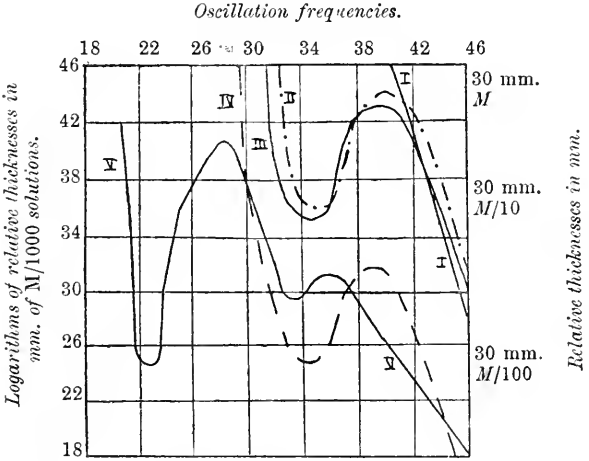
Propionaldehyde.—A *N*/2-alcoholic solution showed a band at about 1/λ 3470 (Fig. 1, III).

Chloral.—A *N*/10-ethereal solution showed a band at about 1/λ 3430 (Fig. 1, IV).

Chloral Hydrate.—A normal alcoholic solution showed no selective absorption. The line of general absorption has been drawn (Fig. 1, I), from which the great transparency of the substance is most strikingly observed.

Glyoxal.—The substance was prepared by distilling commercial glyoxal with phosphoric oxide as described by Harries and Temme (*Ber.*, 1907, **40**, 165). The greenish-yellow vapour condenses to a yellow liquid, which polymerises at once to a white solid in the presence of moisture. A *N*/10-alcoholic solution showed two bands (Fig. 1, V). The less refrangible one at 1/λ 2270 is in the visible regions, and is very strong; and the more refrangible one at 1/λ 3300 is very diffuse.

FIG. 1.



I. *Chloral hydrate.*
II. *Acetaldehyde* (dash and dot line).
III. *Propionaldehyde.*
IV. *Chloral* (dash line).
V. *Glyoxal.*

Acetone.—Stewart and Baly (*loc. cit.*) in alcoholic solution found a large band at 1/λ 3800. The authors have repeated the experiments and confirm this result.

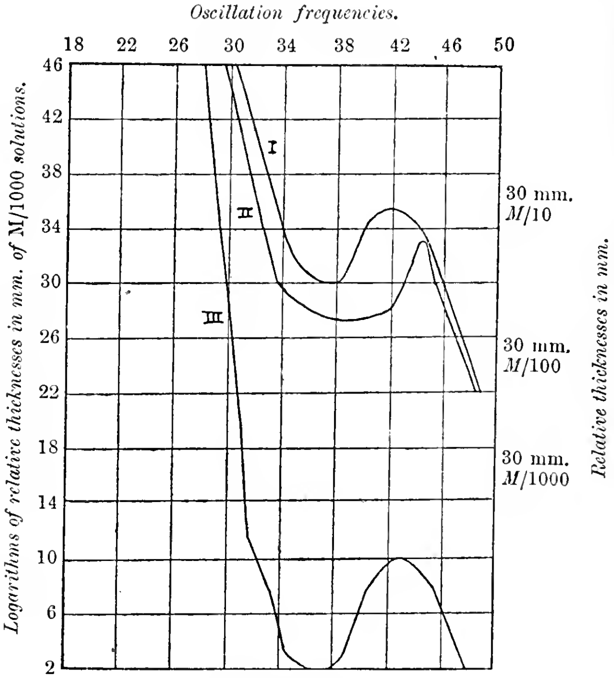
Chloroacetone.—*N*/10-Alcoholic solution showed a very large band (Fig. 2, II), similar to that of acetone in shape, but extending over a larger region of the spectrum and less persistent.

Methyl Ethyl Ketone.—Stewart and Baly (*loc. cit.*) found a band at about 1/λ 3600, and the authors have confirmed this result.

Diethyl Ketone.—*N*/10-Alcoholic solution showed a band at 1/λ 3750 (Fig. 2, I) very similar to that of acetone and of methyl ethyl ketone, but less persistent.

Acetylacetone.—Baly and Desch (Trans., 1904, **85**, 1029) found a large band, and the authors have confirmed this result (Fig. 2, III). The curve has been drawn to show the great absorptive capacity of the substance as compared with the other substances, a result which is also very predominant in the vapour as described below.

FIG. 2.



I. *Diethyl ketone.*
II. *Monochloroacetone.*
III. *Acetylacetone.*

Diacetyl.—Baly and Stewart (Trans., 1906, **89**, 502) describe a strong band at 1/λ 2400, and a rapid extension of the absorption between 1/λ 3400 and 1/λ 4000.

Results of the Solutions.

With the exception of glyoxal and chloral hydrate, the ketones and aldehydes above described exhibit one single large band in the ultra-violet regions. The exceptions are (1) the great transparency of chloral hydrate, and (2) the appearance of a second strong persistent band in the visible regions of the glyoxal solution; and also, according to Baly and Stewart, a strong band in diacetyl in the visible region and a much weaker one in the ultra-violet regions.

Vapours.

Formaldehyde.—The vapour was prepared by heating purified paraformaldehyde and passing the vapour directly into the 200 mm. absorption tube. There was no deposit of the paraformaldehyde on the sides of the quartz ends, so that the radiant energy must have passed through vapour. A series of bands were observed, and the table below gives the measurements of these bands. The bands are wide, and strongest and sharpest in the more refrangible edges. Each band is made up of a considerable number of constituents, some of which can be resolved by means of a magnifier, but they are too close to measure with any degree of accuracy. It is proposed later to use an instrument with a greater dispersion, and a fuller account of the bands will then be submitted. The measurements below are the extent of the wide bands at 16° and 756 mm. pressure when the vapour was in a tube 200 mm. long. Abbreviations: w. = weak; mod.w. = moderately weak; v.w. = very weak; str. = strong; mod.str. = moderately strong; v.str. = very strong.

	λ.	
1.	3530—3505	w.
2.	3430—3410	mod.w.
	3390—3360	mod.str.
3.	3300—3285	,,
	3265—3250	str.
4.	3215—3195	w.
	3185—3150	str.
	3145—3125	,,
	3115—3110	v.w.
5.	3100—3080	mod.str.
	3065—3050	str.
	3045—3030	,,
6.	3025—3015	mod.str.
	3010—2985	,,
	2980—2970	,,
	2968—2960	,,
	2958—2950	v.str.
7.	2940—2930	mod.str.
	2895—2880	str.
	2870—2835	,,
8.	2815—2805	w.
	2800—2785	str.
	2780—2745	,,

The bands may be divided into groups, chiefly triplets, the most refrangible of which is the strongest. The two bands of each of the series 2 and 3 probably represent the stronger bands of similar triplets, the least refrangible being too weak to be seen. A reproduction of the plate is reproduced in Fig. 4, enlarged twice the size from an original negative; the white lines are the images of various copper lines. The numbers above the photograph correspond with the groups numbered in the above table, and the numbers below are approximate positions of wave-lengths.

Acetaldehyde.—The absorption bands of the vapour of acetaldehyde in a 200 mm. tube at various temperatures and pressures.

t°.	Pressure in mm.	
18	761	The rays were absorbed between λ 3010—λ 2750 and then transmitted to about λ 2185.
30	805	The rays were absorbed between λ 3010—λ 2720 and then transmitted to λ 2190.
45	831	The rays were absorbed between λ 3010—λ 2690 and then transmitted to λ 2195.
60	861	The rays were absorbed between λ 3010—λ 2670 and then transmitted to λ 2225.
75	890	The rays were absorbed between λ 3015—λ 2380 and then weakly transmitted to λ 2270.

The vapour shows a strong, wide band, which becomes wider and stronger as the temperature and pressure increase, and the band disappears under general absorption at higher temperatures and pressures. There is no appearance of a series of smaller bands as in the vapour of formaldehyde.

The vapour of acetaldehyde was also studied at a constant temperature of 17° and at varying pressures, namely:

Pressure in mm.	
50	The rays were transmitted to about λ 2110.
92	The rays were transmitted to about λ 2140, but they were rather weak between about λ 2900—λ 2700.
213	The rays were absorbed between λ 3000—λ 2670 and then transmitted to λ 2180.
750	The rays were absorbed between λ 3190—λ 2540 and then transmitted to λ 2210.

That is to say, the large band did not break up into a series of bands at reduced pressures. There is no series of fine bands like those in the vapour of formaldehyde. The band is not unlike the solution band in appearance; although, of course, there is a slight difference in position.

Propionaldehyde.—The absorption spectrum of the vapour of propionaldehyde at various temperatures and pressures in a tube 200 mm. long:

t°.	Pressure in mm.	
18	766	The rays were transmitted to about λ 3100; they were then transmitted very feebly to about λ 2690, and then transmitted to about λ 2180.
30	810	The rays were absorbed between about λ 3160—λ 2580 and then transmitted to λ 2190.

t°.	Pressure in mm.	
45	836	The rays were absorbed between about λ 3290—λ 2550 and then transmitted to λ 2230.
60	866	The rays were absorbed between about λ 3300—λ 2470 and then transmitted to λ 2250.
75	893	The rays were absorbed from about λ 3360, but the series of Cd lines 2329, 2321, 2313, 2288 were just visible.

The vapour therefore exhibits a strong, wide band, which becomes wider and stronger as the temperature increases, and finally disappears under the general absorption. There is no appearance of a series of bands as in the vapour of formaldehyde. The single band is comparable with the solution band, except in the slight difference of position.

Chloral.—The absorption spectrum of the vapour chloral at various temperatures and pressures in a tube 200 mm. long:

t°.	Pressure in mm.	
20	763	The rays were transmitted to about λ 2190, but they were weak between λ 3050—λ 2700.
30	807	The rays were almost completely absorbed between λ 3100—λ 2680 and then transmitted to λ 2260.
45	833	The rays were absorbed between λ 3150—λ 2670 and then transmitted to λ 2240.
60	863	The rays were absorbed between λ 3260—λ 2600 and then transmitted to λ 2260.
75	890	The rays were absorbed between λ 3350—λ 2470 and then very weakly transmitted to λ 2330; the Cd lines 2313, 2321, and 2329 were faintly visible, as well as the Cd line 2573.

The vapour therefore exhibits a strong, wide band, which becomes wider and stronger as the temperature and pressure increase, and finally disappears under the general absorption at higher temperatures and pressures. There is no appearance of a series of bands as in the vapour of formaldehyde. The band is comparable with the solution band, except in position.

Acetone.—The absorption spectrum of the vapour of acetone at various temperatures and pressures in a 200 mm. tube:

t°.	Pressure in mm.	
17	759	The rays were absorbed between λ 2620—λ 2470 and then transmitted to λ 2200.
30	803	The rays were absorbed between λ 2650—λ 2420 and then transmitted to λ 2220.
45	829	The rays were absorbed between λ 2720—λ 2380 and then transmitted to λ 2235.
60	859	The rays were absorbed between λ 2870—λ 2350 and then transmitted to λ 2240.
75	888	The rays were absorbed between λ 2970—λ 2330 and then transmitted to λ 2250.

The vapour shows a strong, wide band, which becomes wider and stronger as the temperature and pressure increase; the band would most probably disappear under general absorption at higher temperatures and pressures. The single band is comparable with the solution band, except in position, where there is a slight difference. There is no appearance of a series of fine bands like those in the vapour of formaldehyde.

Chloroacetone.—The absorption spectrum of the vapour of chloroacetone at various temperatures and pressures in a 200 mm. tube:

t°.	Pressure in mm.	
19	762	The rays were transmitted to λ 2150.
30	806	,, ,, ,, λ 2155.
45	832	,, ,, ,, λ 2160.
60	862	,, ,, ,, λ 2180, but they were weak between λ 3080—λ 2750.
75	891	The rays were absorbed between λ 3100—λ 2720 and then transmitted to λ 2270.
90	922	The rays were absorbed between λ 3180—λ 2580 and then weakly transmitted to λ 2340.

The vapour therefore shows one very strong band, which becomes wider and stronger as the temperature and pressure increase. The band is not unlike the solution band.

Methyl Ethyl Ketone.—The absorption spectrum of the vapour of methyl ethyl ketone at various temperatures and pressures in a 200 mm. tube:

t°.	Pressure in mm.	
19	762	The rays were transmitted to about λ 2140.
30	806	,, ,, ,, λ 2140, but they were rather weak between about λ 2850—λ 2650.
45	832	The rays were absorbed between λ 2900—λ 2600 and then transmitted to λ 2150.
60	862	The rays were absorbed between λ 3030—λ 2500 and then transmitted to λ 2150.
75	891	The rays were absorbed between λ 3100—λ 2420 and then transmitted to about λ 2190.
90	922	The rays were wholly absorbed from λ 3150.

The vapour shows a strong wide band, which becomes wider and stronger as the temperature and pressure increase, and finally disappears under the general absorption at the highest temperature and pressure. The band is comparable with the solution band, except in position, where there is a slight difference.

Diethyl Ketone.—The absorption spectrum of diethyl ketone at various temperatures and pressures in a 200 mm. tube:

t°.	Pressure in mm.	
20	760	The rays were transmitted to λ 2420.
30	804	,, ,, ,, about λ 2770; they were weak from here to about λ 2600 and then were transmitted to about λ 2460.
45	830	The rays were absorbed between about λ 2900—λ 2580 and then transmitted to about λ 2470.
60	860	The rays were absorbed from about λ 3030.
75	889	,, ,, ,, ,, λ 3080.

The vapour therefore shows a fairly wide band, which disappears under the general absorption at the higher temperatures and pressures. The band is comparable with the solution band.

Acetylacetone.—The absorption spectrum of the vapour of acetylacetone at various temperatures and pressures in a 200 mm. tube:

t°.	Pressure in mm.	
18	759	The rays were transmitted to λ 2940.
30	803	,, ,, ,, λ 2940.
45	829	,, ,, ,, λ 2945.
60	859	,, ,, ,, λ 2945.
75	888	,, ,, ,, λ 2945.

The absorption spectrum of the vapour of acetylacetone was also observed at a constant temperature of 18° and at very much reduced pressures. The following notes describe the phenomena.

Pressure in mm.	
19	The rays were absorbed between about λ 2780—λ 2450 and then transmitted to λ 2140.
179	The rays were absorbed between λ 2850—λ 2340 and then transmitted to λ 2155.
324	The rays were absorbed between λ 2890—λ 2230 and then transmitted to λ 2180.
494	The rays were absorbed from λ 2935.
626	,, ,, ,, λ 2945.

The absorptive power of the vapour of this substance is very great, and it is only under considerably reduced pressures that the strong band makes its appearance. This band is very wide and strong at the reduced pressure of 19 mm., and becomes wider at the increased pressures. It is covered up by the general absorption at 494 mm. and 18°, and is comparable with the solution band. The great absorptive power of the substance is apparent both in the alcoholic solution and the vapour.

Glyoxal.—The vapour of glyoxal was introduced into the absorption tube by distilling, with phosphoric oxide, the solid commercial polymeride of glyoxal directly into it as described before. The observations were at various temperatures and pressures, and a considerable number of bands were observed. A greater dispersion will be necessary for more exact measurements of the bands than those given below, and it is proposed shortly to study the vapour of glyoxal with an instrument of greater dispersion. Meanwhile, the bands measured below were those photographed at 18° and 238 mm. pressure, and the source of light was an acetylene flame. They are rather narrow, and usually stronger and sharper on the more refrangible edges: the measurements represent the position on the more refrangible edges.

Abbreviations: v.w. = very weak; narr. = narrow; str. = strong; mod.str. = moderately strong; mod.w. = moderately weak.

	λ.	
	4770	v.w., narr.
	4740	,, ,,
	4715	,, ,,
1	4650	mod.str., narr.
	4635	mod.w., ,,
	4620	v.w., ,,
	4590	,, ,,
	4575	mod.str., ,,
	4565	w., very narr.
	4560	w., narr.
A	4550	str., narr.
	4540	mod.str., narr.
	4510	,, ,,
	4500	,, ,,
	4490	,, ,,
	4480	,, ,,
	4470	w., narr.
	4465	,, ,,
C	4425	mod.str., narr.
	4415	w., narr.
	4410	,, ,,
	4405	v.w., narr.
	4380	mod.str., narr.

		λ.	
		4370	v.w., very narr.
2		4345	mod.str., narr.
		4330	mod.w., ,,
		4290	v.w., ,,
	B	4285	
		4280	,, ,,
		4275	,, ,,
	A′	4265	mod.str., ,,
		4245	,, ,,
		4230	,, ,,
		4225	,, ,,
		4220	v.w., ,,
		4200	mod.str., ,,
		4185	,, ,,
1′	C′	4165	w., narr.
		4155	,, ,,
		4145	,, ,,
		4140	v.w., narr.
		4130	mod.str., narr.
		4110	,, ,,
		4100	,, ,,
		4085	,, ,,

		λ.	
2′		4075	mod.w., narr.
		4055	v.w., ,,
		4045	,, ,,
		4035	,, ,,
		4030	,, ,,
		4010	mod.w., ,,
		3995	,, ,,
		3970	v.w., ,,
		3950	,, ,,
1²	B′	3940	,, ,,
		3935	,, ,,
		3930	,, ,,
		3915	,, ,,
		3900	,, ,,
		3875	,, ,,
		3860	,, ,,
		3850	,, ,,
		3845	,, ,,
		3800	,, ,,
		3785	,, ,,
		3715	,, ,,
		3705	,, ,,
		3465	,, ,,
		3445	,, ,,

The above series of bands are comparable with the single less refrangible solution band $1/\lambda$ 2270 of this substance in that they include the region covered by the solution band. It appears as if the freer vibrations of the vapour molecules are constricted by the solvent, so that only one large band is seen in solution, which breaks up into a series of smaller bands in the vapour. There are also traces of a very weak band extending from about λ 3100—λ 2850. It corresponds with the more refrangible weak solution band; but does not appear to divide up into a series of narrow bands like the more refrangible ones in the visible regions of the spectrum.

Even with the small dispersion used, a fair comparison can be made between several groups of these bands; for example, the bands marked A and A′, B and B′, C and C′, are quite comparable in appearance, and there is a fair comparison to be made in the groups 1, 1¹, and 1² and the groups 2 and 2′. Fig. 3 is a reproduction of an original negative enlarged twice the size, and the numbers

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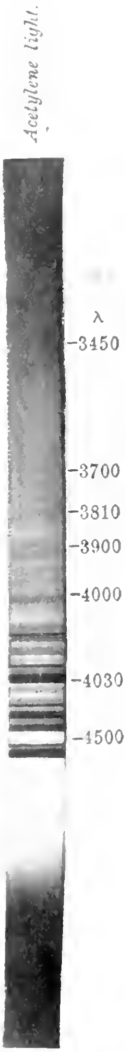

yoxal vapour.

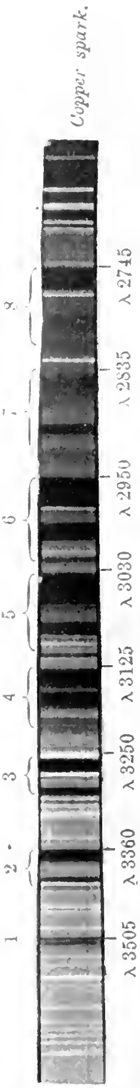

Fig. 4.
Formaldehyde vapour.

Fig. 5.
Diacetyl vapour.

This shows the three more refrangible bands better than the upper one.

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below the photograph are the approximate positions of wavelengths.

Diacetyl.—The vapour was distilled directly into the 200 mm. tube and heated at various temperatures and pressures, and the light of an acetylene lamp was passed through it. The plate showed fine series of fluted bands, which were sharper and stronger on the more refrangible edges. The two least refrangible series were weak, and the three most refrangible ones were even weaker. These fluted bands were made up of a series of still finer constituents, which became weaker on the more refrangible edges. The several constituents of the bands were so closely packed together that it was impossible to measure them with any great degree of accuracy, and it is proposed to study them with an instrument of greater dispersion. The following table contains the width of the fluted bands measured from the most refrangible sharpest and strongest constituent to the least refrangible and weakest at 30° and 800 mm. pressure:

λ 4500—λ 4370 weak
4350— 4275 ,,
4230— 4160 very weak
4145— 4100 ,,
4075— 4020 ,,

These bands are comparable with the less refrangible solution band as described by Baly and Stewart (*loc. cit.*), in that they include the region covered by the least refrangible solution band at 1/λ 2400. The latter opens out into a series of fine fluted bands when the substance is in the vaporous condition. There is also a suggestion of a very weak band extending from about λ 2780—λ 2430, comparable with the rapid extension of the solution curve described by Baly and Stewart (*loc. cit.*). The vapour bands of diacetyl are much weaker or less sharp than those of either formaldehyde or glyoxal. Fig. 5 is a reproduction of one of the negatives enlarged to twice the size of the original.

Results.—The results of measuring the absorption spectrum of the vapours prove that, with the exception of glyoxal, formaldehyde, and diacetyl, each substance has a single band comparable with the solution band except in position. The outstanding fact, however, is the very considerable number of bands in the vapours of formaldehyde, glyoxal, and diacetyl, whereas the solutions of these substances do not show these bands.

Thin Films.

Several of the substances were investigated in thin films; each liquid was enclosed between two quartz plates which were fixed in front of the slit of the spectroscope, and the radiant light passed through for various periods of time. In most cases it was impossible to obtain a thick enough film, owing to the small viscosity, and to the volatility of the substances.

Chloral.—During one minute's exposure the rays were absorbed between about λ 3160 and λ 2530, and then transmitted to about λ 2440. The thickness of the film was less than 0·1 mm.

Diethyl Ketone.—During one minute's exposure the rays were absorbed between about λ 3050 and λ 2420, and then transmitted to about λ 2280. The thickness of the film was about 0·8 mm.

Acetylacetone.—During five minutes' exposure the rays were absorbed between about λ 3020 and λ 2340, and then transmitted to about λ 2130. For this observation it was necessary to squeeze a drop of the liquid tightly between two quartz plates.

The phenomena are not unlike the solution bands, and there is no resolution of the single band into a series of smaller bands. It may be well to draw attention to some previous investigations by one of us (Purvis, Trans., 1910, **97**, 692, 1035, 1547) with regard to the absorption of thin films of pyridine and of aniline and other compounds. No bands were observed in films of these substances so thin as 0·01 mm. and of about 0·001 mm. The observations meant that with the same source of light of the same intensity, and the same distance from the slit, as were used for the solutions and the vapours, no light could get through to show specific absorption, and only general absorption was observed. No inference was to be drawn that no specific absorption was ever possible in thin films, for with a much stronger source of light placed nearer the slit, or in some cases by tightly passing the film between quartz plates, specific absorption can be observed, and such bands are comparable with the solution bands, the only difference being one of position.

Discussion of Results.

The general results of this comparative study are to confirm previous observations that the physical conditions of any vibrating system influence the absorption of light. The outstanding facts are: (1) the considerable number of absorption bands found in the vapours of formaldehyde, glyoxal, and diacetyl, as compared with the one or two in the solutions and the thin films of these substances. (2) The complete disappearance of the solution band of chloral in solutions of chloral hydrate; and (3) the general resemblance of the solution bands with the vapour bands in the other ketones and aldehydes here investigated.

Until recently the phenomena of light absorption have been explained by a hypothetical vibrational tautomerism (Stewart and Baly, Trans., 1906, **89**, 489, 502), which, in the case of the ketones, has been represented by the change

$$\cdot CH_2\cdot\underset{\substack{\| \\ O}}{C}\cdot \quad \rightleftarrows \quad \cdot CH{:}\underset{\substack{| \\ OH}}{C}\cdot$$

More recently, however, it has been found that this explanation does not meet all the facts (Lowry and Desch, Trans., 1909, **95**, 807), and it has therefore been necessary to suggest another theory to account for the observed facts. That the results indicated above cannot be explained by any kind of periodic tautomeric change is evident from the bands observed in formaldehyde vapour and in chloral, where no such change is possible; and in the other aldehydes where it is not supported by any chemical evidence.

Since it cannot be disputed that the bands are due to vibrations of some kind, and since it is shown that these vibrations are not of the kind mentioned above, it is suggested that the vibrations in the aldehydes and ketones take place primarily within the C:O group, which may be termed the "oscillation centre" for this type of substance. This suggestion is supported by the observation that when the C:O group disappears, as in chloral hydrate, there is no selective, and comparatively little general absorption.

If the vibrations have their origin within the C:O group it appears that these must be vibrations of electrons, and Drude's theory ("Theory of Optics," Sect. II., Ch. V.) may be applied with some modification. According to this theory the electrons vibrate in accordance with the law expressed by the following equation (the notation of the original is here simplified):

$$l.\frac{d^2x}{dt^2} + r\frac{dx}{dt} + cx = E\cos pt.$$

In this equation, x is a co-ordinate denoting the displacement of the system from its equilibrium position; l is the inertia constant, which depends partly on the mass, but chiefly on the self-induction of the electron; the second term represents the force of friction; and the third the rigidity of the system; and $E\cos pt$ is the periodic disturbing force, due to the light. The modification from Drude's theory lies in the fact that l cannot be assumed constant for all electrons; and defined as above it may vary from substance to substance. It is not desirable here to develop fully the results of this equation with the necessary modifications, but it is hoped to publish them shortly in another place. It may be stated, however, that the frequency of the natural vibrations is proportional to $\sqrt{c/l}$, and the sharpness of the bands depends on the smallness of r^2c/l. Further, it will be assumed that r and c, and possibly l, increase on passing up a homologous series.

The following is an indication of a possible interpretation of the results obtained on the lines indicated above. Taking first the vapour in formaldehyde, r^2c/l is small comparatively speaking, and consequently the bands due to the different kinds of electrons do not merge into one another. We therefore have a series of lines. In other aldehydes and ketones the above expression has increased, and the separate bands merge into one wide one. It must be remembered, however, that by a careful adjustment of physical conditions it is possible that these large bands may break up into rather wide, separate bands by the use of greater dispersion than that with which the above results were obtained.

The change in the position of the band may be explained on similar lines. That the rigidity of the C:O group in formaldehyde is small is suggested by the extreme ease with which this substance polymerises; c is, therefore, small for this substance as compared with acetone, for example; and the hypothetical increase of l on passing to the latter may not compensate for this. Consequently the absorption shifts towards the more refrangible part on passing from formaldehyde to acetone.

The general effect of the solvent is to cause broad bands to appear where the vapours showed a series of fine lines, as, for example, in the well-known case of benzene. This is readily understood on the above theory, for the solvent will evidently cause the friction to increase. It will at the same time affect l, that is, change the position of the band.

Turning now to the substances containing two C:O groups; for example, glyoxal, two explanations are possible; one is as follows: that the less refrangible band is due to the complex $\begin{matrix}\mathrm{C:O}\\ |\\ \mathrm{C:O}\end{matrix}$, and the more refrangible band to vibrations originating in the C:O groups independently.

Another explanation can be derived from an extension of the theory indicated above. It is necessary to introduce a term into the fundamental equation to denote the mutual induction of the two systems of electrons.

The equations then become (it is evident that the two centres are symmetrically situated):

$$l\frac{d^2x}{dt^2} + m\frac{d^2y}{dt} + r\frac{dx}{dt} + cx = \cos pt.$$

$$m\frac{d^2x}{dt^2} + l\frac{d^2y}{dt} + r\frac{dy}{dt} + cy = E\cos pt.$$

From these equations it may be deduced that there will be two bands, which may be approximately derived from the two equations.

$$(l + m)\frac{d^2x}{dt^2} + r\frac{dx}{dt} + cx = E\cos pt. \quad (A.)$$

$$(l - m)\frac{d^2x}{dt} + r\operatorname{cosec}\eta\frac{dx}{dt} + cx = E\cos pt. \quad \text{wherein} \quad \tan\eta = \frac{r}{2pm} \quad (B.)$$

It follows from these that the frequency of the band due to A will be less than that of the band due to B, whilst the latter will be more diffuse, since $\frac{cr^2}{(l+m)}$ is less than $\frac{cr^2 \operatorname{cosec}^2\eta}{(l-m)}$. The ratio $l : m$ may be calculated from the positions of the bands; for glyoxal $m = 0{\cdot}4l$ roughly.

Since m will depend primarily on the distance between the two oscillation centres, for acetylacetone it will be smaller than for glyoxal; hence, bearing in mind the increased diffuseness of the band due to the presence of methyl groups, it is not surprising to find that the bands merge into one another, producing the exceedingly broad band found.

It must, however, be admitted that the strength of the band of acetylacetone is not fully explained by either of the above hypotheses.

The authors desire to thank the Government Grant Committee of the Royal Society, by whose generosity the cost of this research was partly defrayed.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CXCIII.—*The Bromination of Phenol. 2:4- and 2:6-Dibromophenol.*

By FRANK GEORGE POPE and ARTHUR SAMUEL WOOD.

CONSIDERABLE quantities of 2:4- and 2:6-dibromophenol being required for an investigation now in progress, it was found that the preparation of these compounds was, as a rule, attended by considerable difficulty, and that the yields obtained were in most cases rather small, more especially in the case of 2:6-dibromophenol.

Körner (*Annalen*, 1866, **137**, 205) prepared 2:4-dibromophenol by the direct bromination of phenol in the cold, whilst Peratoner

(*Gazzetta*, 1886, **16**, 402) obtained it by the heating of 3:5-dibromosalicylic acid with dilute sulphuric acid at 220—230°. Somewhat later, Schryver (Trans., 1899, **75**, 618) showed that it could be obtained by direct bromination of phenol in carbon disulphide solution in the presence of some aluminium chloride, and Hewitt (Trans., 1904, **85**, 1225), by suspending phenol in 75 per cent. sulphuric acid and adding bromine, succeeded in obtaining a 93 per cent. yield of the 2:4-dibromo-compound.

After trying the several methods above mentioned, we found that 2:4-dibromophenol could be most rapidly prepared if the bromination of phenol were carried out in the presence of hydrobromic acid. In one experiment 23·5 grams of phenol were suspended in 70 grams of hydrobromic acid (D 1·49), and the mixture was slightly warmed until the phenol melted. The solution was then cooled in a freezing mixture to −10°, and 80 grams of bromine dissolved in 40 grams of hydrobromic acid were run in very slowly, the temperature being kept below 0°. Bromine was absorbed very slowly, and when about half had been added, all the phenol had liquefied. The temperature of the mixture was now allowed to rise to 0°, the remainder of the bromine solution added more rapidly, and the mixture allowed to remain for one hour. At the end of this time the reaction mixture was heated slightly (to about 30°) until the colour of the bromine just disappeared; and then put aside for three hours. The supernatant hydrobromic acid was run off from the 2:4-dibromophenol, diluted somewhat with water, and recovered by distillation. The dibromophenol was melted under water, washed several times with small quantities of warm water by decantation, and finally dried in a vacuum desiccator. The yield of the crude product was 55 grams (87—88 per cent.), and it melted at 37·6°. After recrystallisation from light petroleum, 2:4-dibromophenol melts at 40° (corr.).

2:4-Dibromophenol crystallises in long, colourless needles. The melting point as given in the earlier preparations by different investigators is 34—35° (Hewitt); 35—36° (Peratoner); 40° (Körner). The lower values are probably due to the fact that 2:4-dibromophenol apparently retains traces of water which are difficult to remove, for on distillation of a specimen which had been kept over sulphuric acid in a vacuum for two weeks a small quantity of water was obtained as a first distillate. For further purification we recommend distillation of the bromo-compound under diminished pressure, and then recrystallisation from light petroleum. Working in this way, a product is obtained which melts sharply at 40° (corr.), and boils at 177°/17 mm.

The 2:4-dibromophenol thus obtained was characterised by the preparation of various derivatives. The benzoate prepared by the Schotten-Baumann reaction crystallises from alcoholic solution in long, colourless needles, which melt at 97·5° (corr.), and is identical with the compound prepared by Autenrieth and Mühlinghaus (*Ber.*, 1907, **40**, 747) by the action of phosphorus pentabromide on phenyl benzoate. (Found, Br=44·40. Calc., Br=44·94 per cent.)

The p-*nitrobenzoate* was prepared in a similar manner from 2:4-dibromophenol and *p*-nitrobenzoyl chloride. It crystallises from glacial acetic acid in almost colourless groups of needles, and is readily soluble in benzene or glacial acetic acid, but is almost insoluble in light petroleum. It melts at 183·5° (corr.):

0·2061 gave 0·1911 AgBr. Br=39·45.

$C_{13}H_7O_4NBr_2$ requires Br=39·9 per cent.

The methyl ether was obtained by warming the dibromophenol in alkaline solution with an equivalent amount of methyl sulphate. It gradually separates from the reaction mixture as an oil. The oil was separated and well washed with water, and cooled in a freezing mixture. The crystalline mass was finally dried over sulphuric acid in a vacuum, and then crystallised from light petroleum. It separates from the solvent in colourless, transparent prisms, which melt at 61·3° (corr.). Körner, by methylating with methyl iodide in the presence of alkali, obtained the methyl ether, which melted at 59°.

The *ethyl ether* was prepared by dissolving 5 grams of the dibromophenol in alcohol, adding to the solution 0·5 gram of sodium dissolved in 15 grams of alcohol, and running in 3·5 grams of ethyl iodide. The whole was heated under reflux for three hours, and the excess of alcohol then distilled off. The residue was washed with water and cooled to 0° to induce solidification. It was finally dried under diminished pressure, and crystallised from light petroleum, from which it separates in transparent, colourless, rhombic plates, melting at 53·3°:

0·2041 gave 0·2766 AgBr. Br=57·66.

$C_8H_8OBr_2$ requires Br=57·14 per cent.

The *acetyl* derivative was prepared by heating 5 grams of the dibromophenol with 30 grams of acetic anhydride and 5 grams anhydrous sodium acetate for three hours. The excess of acetic anhydride was destroyed by keeping for some time with dilute alcohol, and the product gradually became solid. No convenient solvent could be obtained for crystallisation purposes, and the acetate was finally purified by distillation in a current of steam. It separates from the distillate in small, colourless needles, which melt at 36° (corr.):

0·3993 gave 0·515 AgBr. Br=54·86.

$C_8H_6O_2Br_2$ requires Br=54·42 per cent.

The nitro-derivative was prepared by dissolving 5 grams of the dibromophenol in 40 grams of glacial acetic acid, cooling the solution to 0°, and then running in 1 c.c. of fuming nitric acid dissolved in 5 grams of glacial acetic acid slowly and with vigorous stirring. The mixture was kept in ice for half an hour, and then poured into water. The precipitate was collected, washed, and recrystallised from glacial acetic acid, from which it separates in small, yellow prisms, melting at 117·5° (corr.). It is thus identical with the product obtained by Körner (*Zeitsch. Chem.*, 1868, 323) by the bromination of *o*-nitrophenol, and is 2:4-dibromo-6-nitrophenol.

2:6-Dibromophenol has been obtained in small yield by the distillation of tetrabromophenolphthalein with concentrated sulphuric acid (Baeyer, *Annalen*, 1880, **202**, 138); by the action of ethyl nitrite on 2:6-dibromo-*p*-aminophenol (Möhlau, *Ber.*, 1882, **15**, 2494; Schryver, Trans., 1899, **75**, 618), or by the action of nitrous acid on 2:6-dibromoaniline (Heinichen, *Annalen*, 1889, **253**, 281). After trying the several methods, we drew the conclusion that it could be best obtained by the elimination of carbon dioxide from 3:5-dibromo-4-hydroxybenzoic acid. This acid has been previously prepared by Balbiano (*Gazzetta*, 1883, **13**, 69) by the distillation of the sodium salt of dibromoanisic acid with lime; by Alessi (*ibid.*, 1885, **15**, 243) by the decomposition of dibromoanisic acid with hydriodic acid; by Paal and Kromschröder (*Ber.*, 1895, **28**, 3236) by the oxidation of the corresponding aldehyde with dilute potassium permanganate in alkaline solution; and by Robertson (Trans., 1902, **81**, 1482) by brominating the acid in acetic acid solution in the presence of iodine, and pouring the product of reaction into sodium hydrogen sulphite solution. Robertson obtains an 80 per cent. yield of the dibromo-acid in this manner, but we find that if the method of preparation is modified in the following manner a yield of 90 per cent. is possible, even after allowing for the tribromophenol formed in small quantity by replacement of the carboxyl group in a portion of the acid by bromine.

55·2 Grams of *p*-hydroxybenzoic acid were stirred into 1600 grams of 75 per cent. sulphuric acid, and the mixture was cooled to 0°, so as to avoid the formation of much tribromophenol during the course of the reaction. 128 Grams of bromine dissolved in 128 grams of glacial acetic acid were also cooled to 0°, and the solution run into the suspension of the hydroxybenzoic acid with vigorous stirring, the temperature being kept below 5°. The reaction proceeds slowly, and when about half the bromine is added the mass sets to a stiff paste. The remainder of the bromine solution is now run in more rapidly, and the mixture stirred thoroughly in order that the bromine may be well diffused throughout the mass. During this operation a copious evolution of hydrogen bromide takes place. The reaction mixture is allowed to remain for one week, with occasional stirring, during which time the colour of the bromine gradually disappears. It is then poured into 4 litres of water, allowed to remain for about half an hour, collected, washed, and dried at about 80—100°. The crude acid obtained in this way, on drying under a glass funnel, was found to yield a small quantity of a crystalline sublimate, which melted at 89°, and was therefore most probably a little tribromophenol. To remove this, the crude acid was heated under reflux for half an hour with light petroleum, collected, and dried. The acid is readily soluble in alcohol, glacial acetic acid, ethyl acetate, or epichlorohydrin, crystallising from the latter solvent in fine, colourless needles, which melt at 268°. (Found, Br = 54·36. Calc., Br = 54·05 per cent.)

Consequently, taken in conjunction with the melting-point determination, these figures show that the acid is 3:5-dibromo-4-hydroxybenzoic acid. The crystals obtained on evaporation of the light petroleum extract, on recrystallisation melted at 95—96°, and hence consisted of 2:4:6-tribromophenol. The acid was characterised by conversion into its methyl ester, which melted at 126°, and into its ethyl ester, which melted at 108° (Robertson gives m. p. 99°).

Various methods were used for the elimination of carbon dioxide from the acid, the earlier experiments being conducted by heating 5 grams of the acid with 25 grams of a 5 per cent. solution of sulphuric acid to 150—160° for four hours in a sealed tube. The tube was then opened in order to relieve the pressure, sealed again, and heated for a further four hours.

The reaction mixture was then distilled in a current of steam, and the crude 2:6-dibromophenol obtained melted at 51—52°. A greater concentration of sulphuric acid in the tube slowed the reaction very greatly.

The effect of piperidine was then tried, 5 grams of the acid being heated with 25 grams of water and 15 drops of piperidine for two hours at 150°. The dark-coloured solid obtained was acidified and distilled in a current of steam, when 2:6-dibromophenol was obtained in almost theoretical yield, the crude product melting at 52—53°. Finally, it was found that exceedingly good yields were obtained by heating the acid with water alone to about 160° for several hours, but in consequence of the high pressures produced the tubes burst in the majority of the preparations. To obviate the loss of material it was found that the presence of sodium hydroxide prevented the bursting of the tubes, but that then the yield of material decreased. Thirty grams of the acid were heated with 200 c.c. *N*-sodium hydroxide solution for 1½ hours at 165°, the product acidified, and distilled in a current of steam, when 13 grams of 2:6-dibromophenol, crystallising in long, slender needles, melting at 56—57° and boiling at 162°/21 mm., were obtained. (Found: Br = 64·0. Calc., Br = 63·5 per cent.)

The dibromophenol was characterised by conversion into its nitro-derivative, the nitration being carried out in glacial acetic acid solution at 0°, using fuming nitric acid in slight excess. The nitro-compound crystallises from dilute alcohol in small, yellow prisms, which melt at 144—145°, and is thus 2:6-dibromo-4-nitrophenol. The earlier literature dealing with this compound state that it decomposes at temperatures slightly above its melting point, but we find that it can be heated to a much higher temperature without decomposing, thus confirming an observation of van Erp (*Rec. trav. chim.*, 1910, [ii], **14**, 187) that it does not decompose at 180°. The decomposition at the melting-point temperature seems to be more apparent when the substance is prepared by brominating *p*-nitrophenol in acetic acid solution.

The *methyl ether* of 2:6-dibromophenol was obtained by dissolving 5 grams of the phenol in 20 c.c. of methyl alcohol, and adding to the solution 1 gram of sodium dissolved in 15 c.c. of methyl alcohol, and then 5·6 grams of methyl iodide. The reaction mixture was heated under reflux for eight hours, and the excess of alcohol distilled off. The residue was then warmed with sodium hydroxide solution to remove the unchanged phenol, washed with water, and distilled under diminished pressure. The ether distils as a colourless oil, which boils at 143—145°/34 mm., and when cooled in a freezing mixture solidifies to a mass of colourless needles which melt at about 13°. It possesses an odour resembling that of anisole, but much more penetrating, and is readily soluble in all the more common organic solvents:

0·2482 gave 0·3484 AgBr. Br = 59·74.

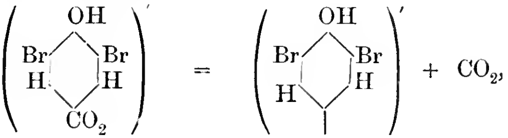
$C_7H_6OBr_2$ requires Br = 60·15 per cent.

The *ethyl ether* was prepared in a similar manner, and after being well washed, solidified directly when placed in a freezing mixture to a mass of colourless crystals, which melt sharply at 40·6°. Its odour is very penetrating and persistent, and it is readily soluble in all the ordinary organic solvents:

0·2043 gave 0·2762 AgBr. Br = 57·53.

$C_8H_8OBr_2$ requires Br = 57·14 per cent.

We are inclined to the opinion that the elimination of carbon dioxide from 3:5-dibromo-4-hydroxybenzoic acid is an ionic reaction for the rate of elimination is slower the greater the concentration of the mineral acid present. If water alone is used, the reaction is more rapid, whilst in the presence of bases or alkali hydroxides it is still more rapid, probably due to the increasing concentration of the acyl ions of the organic acid. It is thus probable that the reaction is to be represented as



In conclusion, we wish to express our thanks to the Research Fund Committee of the East London College for a grant in aid of this investigation.

East London College,
University of London.

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

Whinfield,
Salcombe,
S. Devon.
Sept. 16*th*, 1912.

Gentlemen,

I have the honour to forward the Annual Report of the International Committee on Atomic Weights for 1913, together with a Table of Atomic Weights, which are submitted for publication in the Society's Transactions and Proceedings, as hitherto.

The Report draws attention to all the atomic-weight determinations which have been published since the date of the preceding Report, but the only alteration suggested in the table which accompanied last year's Report is the inclusion of the element holmium, with Ho=163·5, as the result of the work of Holmberg.

I am, Gentlemen,
Your obedient Servant,
T. E. Thorpe.

The Hon. Secretaries,
The Chemical Society,
Burlington House,
London, W.

Annual Report of the International Committee on Atomic Weights, 1913.

Since the annual report for 1912 was prepared, a number of important memoirs on atomic weights have appeared. There are also one or two earlier researches which were received too late to be noticed at the proper time. These investigations may be summarised as follows:

Nitrogen.—Wourtzel (*Compt. rend.*, 1912, **154**, 115), by oxidising NO to N_2O_4, has redetermined the ratio between nitrogen and oxygen. Five concordant measurements give, in mean, N=14·0068.

Potassium and Chlorine.—Staehler and Meyer (*Zeitsch. anorg. Chem.*, 1911, **71**, 368) have made careful analyses of potassium chlorate, with special precautions against contamination by the chloride. Their final series gives KCl=74·5551, whence K=39·097 and Cl=35·458. For a discussion of their results, see also Guye (*J. Chim. phys.*, 1912, **10**, 145), who concludes that the impurity above mentioned was, if not completely, at least sufficiently eliminated to be practically negligible.

Fluorine.—McAdam and Smith (*J. Amer. Chem. Soc.*, 1912, **34**, 592) have published two preliminary determinations of the atomic weight of fluorine. Sodium fluoride was converted into chloride by heating in dry, gaseous hydrochloric acid, and from the ratio between the weights the atomic weight was calculated. The two values found are: F=19·0176 and 19·0133.

Phosphorus.—From analyses of phosphorus tribromide, Baxter, Moore, and Boylston (*Proc. Amer. Acad.*, **47**, 585; *J. Amer. Chem. Soc.*, 1912, **34**, 259) find, in mean of three series, P=31·027 when Ag=107·88. This agrees fairly well with the former work of Baxter and Jones on silver phosphate. Further work on phosphorus trichloride is promised.

Mercury.—Easley and Brann (*J. Amer. Chem. Soc.*, 1912, **34**, 137), by analyses of mercuric bromide, find Hg=200·64. This confirms the previous work of Easley on the chloride.

Selenium.—Kuzma and Krehlik (*Trans. Bohemian Acad. of Emperor Francis Joseph*, 19, No. 13, 1910. Data furnished to the committee by Professor B. Brauner) have redetermined the atomic weight of selenium by reduction of SeO_2 with SO_2. The mean of ten determinations is Se=79·26.

Tellurium.—Harcourt and Baker (Trans., 1911, **99**, 1311) have thrown doubt upon the work of Flint, who claimed to have split up the supposed element into two fractions of different atomic weight. They repeated his method of fractionation, and from the fourth fraction, found Te=127·54. This agrees with the figure found by Baker and Bennett in 1907. Similar fractionations have been carried out also by Pellini (*Atti R. Accad. Lincei*, 1912, [v], **21**, i, 218), who likewise failed to find any indication of a tellurium of low atomic weight.

Radium.—Hönigschmid (*Monatsh.*, 1912, **33**, 253), by careful analyses of relatively large quantities of radium chloride, finds Ra=225·95. On the other hand, Whytlaw-Gray and Ramsay (*Proc. Roy. Soc.*, 1912, **86**, *A*, 270), using very small quantities of material, and converting the bromide into the chloride, find Ra=226·36, in agreement with previous work by Madame Curie and Thorpe. Until the discordance between Hönigschmid's low value and the higher is explained, it is undesirable to change the figure given in the table.

Tantalum.—The determinations of this atomic weight by Chapin and Smith (*J. Amer. Chem. Soc.*, 1911, **33**, 1497) were made by the hydrolysis of $TaBr_5$. The mean of eight determinations gave Ta=181·80, a figure somewhat higher than that found by Balke from similar analyses of the pentachloride.

Iridium.—Hoyermann (*Sitzungsber. phys. med. Soz. Erlangen*, **42**, 278), by five reductions of $(NH_4)_2IrCl_6$ in hydrogen, finds Ir=192·613.

Holmium.—Six determinations of the atomic weight of holmium by Holmberg (*Zeitsch. anorg. Chem.*, 1911, **71**, 226), gave Ho=163·45. The well known sulphate method was employed.

There are also approximate determinations of the atomic weights of lead, zinc, and copper by Pecheux (*Compt. rend.* 1912, **154**, 1419), and of calcium by Oechsner de Coninck (*Compt. rend.*, 1911, **153**, 1579). The figures obtained are not conclusive enough to justify their use in the table, for the methods employed were not of great accuracy.

Only one change is recommended in the table for 1913, namely, the insertion of holmium, for which, hitherto, no good atomic-weight determination has been available. Two or three other alterations of small importance might be made, but it seems undesirable to make changes too frequently.

(*Signed*)

F. W. CLARKE.
T. E. THORPE.
W. OSTWALD.
G. URBAIN.

1913.

International Atomic Weights.

		O=16.			O=16.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·88	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Niton (radium emanation)	Nt	222·4
Bismuth	Bi	208·0	Nitrogen	N	14·01
Boron	B	11·0	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·00	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·6
Chlorine	Cl	35·46	Radium	Ra	226·4
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·5	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
Erbium	Er	167·7	Selenium	Se	79·2
Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	69·9	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·07
Glucinum	Gl	9·1	Tantalum	Ta	181·5
Gold	Au	197·2	Tellurium	Te	127·5
Helium	He	3·99	Terbium	Tb	159·2
Holmium	Ho	163·5	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·4
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	119·0
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·84	Tungsten	W	184·0
Krypton	Kr	82·92	Uranium	U	238·5
Lanthanum	La	139·0	Vanadium	V	51·0
Lead	Pb	207·10	Xenon	Xe	130·2
Lithium	Li	6·94	Ytterbium (Neoytterbium)	Yb	172·0
Lutecium	Lu	174·0	Yttrium	Yt	89·0
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·6			

CXCIV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XVIII. The Effect of Inorganic Salts on the Rotation of Ethyl Tartrate in Aqueous Solution and in the Homogeneous Condition.*

By THOMAS STEWART PATTERSON and DUNCAN GEDDES ANDERSON, B.Sc.

IN a paper published a few years ago, Patterson and McMillan (Trans., 1908, **93**, 1049) described an experiment in which to 10 grams of a $p=50$ aqueous solution of ethyl tartrate there was added, on the one hand, 1 gram of thiocarbamide, and, on the other, 1 gram of ammonium thiocyanate. Whilst the rotation of the aqueous solution alone was $\alpha_D^{20\cdot2}$ $+9\cdot73°$, that of the thiocarbamide solution was α_D^{19} $+10\cdot006°$, and that of the ammonium thiocyanate solution, $\alpha_D^{19\cdot2}$ $+5\cdot26°$. The addition of the thiocarbamide thus raises the rotation of the ethyl tartrate solution, whilst the addition of the ammonium thiocyanate depresses it, the diminution of rotation in the latter case being very striking indeed. The experiment suggested to us a more complete investigation of the effect of the presence of inorganic salts on the rotation of aqueous solutions of ethyl tartrate, and we now give below an account of some work which we have recently carried out in this direction. The problem is, of course, a special case of the influence of mixed solvents on the rotation of an active substance, and Rimbach (*Zeitsch. physikal. Chem.*, 1892, **9**, 698), in a paper dealing with the influence of certain pairs of mixed solvents on the rotation of camphor and of turpentine, describes also the influence of calcium chloride—which is very great—and of magnesium chloride—which is almost nil—on the rotation of dextrose in aqueous solution. The question of the effect of mixed organic solvents on the rotation of ethyl tartrate has been examined by Patterson and Montgomerie (Trans., 1909, **95**, 1128), and whilst the experiments recorded here were being performed there appeared a paper by Stubbs (Trans., 1911, **99**, 2265) on the influence of inactive electrolytes on the optical activity of *l*-malic acid in aqueous solution, which may be consulted for numerous references to other work bearing on the subject.

In commencing an investigation of this kind it is necessary, unless the experiments are to be very comprehensive, to consider the problem of what are to be regarded as suitable conditions for the comparison of different solutions, which may be made up of similar strength as regards percentage composition by weight, or may be prepared by what is called the volume-normal or by the weight-normal method, or in other ways. According to the results recorded by Patterson and Montgomerie (*loc. cit.*, pp. 1131, 1134—1135), the effect of one of the constituents of a mixed solvent appears to be closely proportional to the mean of its percentage by weight and by volume; at least, the properties of such a solution as regards rotation are more nearly additive for this than for other assumptions, but a method of preparing solutions based on this observation would be difficult to realise where one constituent of a solvent was solid, and partly for that reason, and partly because it seemed likely that our results would afford interesting material for comparison with those of H. E. Armstrong, we decided to make up our solutions according to his method. We therefore keep the quantity of ethyl tartrate and of water constant in each solution, adding then equivalent proportions of the different inorganic salts.

The substances used were the ordinary pure salts, once recrystallised, dried, and kept in a vacuum desiccator until required. In the case of such as contained water of crystallisation, like the bromide, iodide, and acetate of sodium, the water was driven off by moderate heating, and the anhydrous condition of the salt established by analysis. In making up the solutions, 5 c.c. of ethyl

TABLE I.

Effect on the Rotation of a Solution of 5·92 *grams of Ethyl Tartrate and* 50 *grams of Water due to the Addition of Various Salts.*

Salt added.	Weight of salt added ($\frac{1}{10}$ gram-mol. weight).	p.	$\alpha_D^{26°}$.	Change of $\alpha_D^{26°}$ due to addition of salt.	$d_4^{26°}$.	$[\alpha]_D^{26°}$.	Change of $[\alpha]_D^{26°}$ due to addition of salt.
None	—	10·59	+2·85°	—	1·021	+26·37°	—
Ammonium chloride..	5·35	9·66	2·28	−0·57°	1·046	22·56	−3·81°
Sodium ,, ..	5·85	9·58	2·12	0·73	1·088	20·32	−6·05
Potassium ,, ..	7·46	9·34	2·04	0·81	1·097	19·59	−6·78
Ammonium nitrate ...	8·00	9·26	2·26	0·59	1·068	22·50	−3·87
Sodium ,, ...	8·50	9·19	2·03	0·82	1·110	19·06	−7·31
Potassium ,, ...	10·11	8·97	1·94	0·91	1·119	19·34	−7·03
Sodium iodide.........	14·99	8·35	1·63	1·22	1·201	16·26	−10·11
Potassium ,, ...	16·60	8·16	1·65	1·20	1·211	16·69	−9·68
Sodium bromide	10·29	8·94	2·00	0·85	1·127	19·86	−6·51
Potassium ,, ...	11·90	8·73	1·85	1·00	1·151	18·41	−7·96
Ammonium sulphate.	13·21	8·56	1·81	1·04	1·129	18·73	−7·64
Potassium thiocyanate	9·72	9·02	1·70	1·27	1·091	17·28	−9·09
Sodium chlorate	10·65	8·89	1·89	0·96	1·132	18·78	−7·59
Sodium acetate.........	8·4	9·23	1·83	1·02	1·087	18·25	−8·12
Carbamide	7·6	9·32	2·69	0·16	1·058	27·29	+0·92
Barium chloride	6·943 ($\frac{1}{50}$ gram-mol. weight)	9·42	1·48	1·334	1·127	13·94	−12·43

tartrate were delivered from a pipette into a flask of about 70 c.c. capacity, and the weight of the ester was adjusted exactly to 5·92 grams. Into another flask of similar capacity, 1/10 of a gram-molecular weight of the salt under investigation was weighed, 50 c.c. of distilled water being then added from a pipette. The solutions are thus practically 2*N*. The contents of the two flasks were thoroughly mixed by pouring from one to the other several times, and the rotation and density of the resulting solution were determined at a temperature of 26°. For comparison, the rotation and density of a solution of 5·92 grams of ethyl tartrate in 50 c.c. of water were also determined. The results obtained are given in table I (p. 1834).

The rotation of ethyl tartrate is greatly raised by solution in water, and it will be seen at once that this effect is counteracted by the addition of the salts; in every case the observed rotation of the mixed solution is lower than that of the aqueous ethyl tartrate without addition, and in every case, except that of thiocarbamide, the specific rotation is also depressed, in most instances to a considerable extent. That there is distinct regularity in these results will best be seen from table II, in which the depression of the specific rotation is shown for each inorganic salt used, and in such a manner as to admit of easy comparison. It may be noted in passing that the specific rotations of the solutions are proportional to the rotations which would be observed in tubes of equal cross-section—but slightly different length—filled with the whole volume of each solution. The different volumes of the added salts and any changes of volume on mixing are thus taken into account.

TABLE II.

Depression of Specific Rotation at 26°.

	Cl.	Br.	I.	NO_3.	SO_4.	NCS.	ClO_3.	OAc.
NH_4 ……	3·81°	—	—	3·87°	7·64°	—	—	—
Na ………	6·05	6·51°	10·11°	7·31	—	—	7·59°	8·12
K…………	6·73	7·96	9·68	7·03	—	9·09°	—	—

Comparing first the effect of ammonium, sodium, and potassium salts, it is clear that the influences of the two last are nearly equal and considerably greater than, in fact, nearly twice as great as, that of the corresponding ammonium salt, but we have only examined two series, the chlorides and the nitrates. It will be noticed also that ammonium sulphate has an effect almost exactly double that of the chloride or nitrate, corresponding, doubtless, with its bivalent character.

Sodium chloride and bromide produce smaller depressions than potassium chloride and bromide, but in the iodides and nitrates the effect is in the opposite sense. Potassium chlorate was not sufficiently soluble to be included in the above table, but in $2N/5$-concentration it causes a slightly greater depression than sodium chlorate in a solution of corresponding strength (see below).

As regards the negative radicles it will be seen that the chlorides produce least depression, then come the bromides or nitrates, the order in these two cases being different for the sodium and potassium salts, then probably the chlorates, followed by the thiocyanates, the acetates, and finally the iodides, which have the greatest effect of the salts used.

Our results show, in general, a very remarkable similarity to those recorded by Stubbs for the effect of electrolytes on the rotation of solutions of *l*-malic acid, the resemblance extending even to what might be called the abnormalities; thus, although Stubbs observed that the magnitude of the effect increased from the ammonium through the sodium to the potassium salts, still, in the nitrates he found, as we do, that in his stronger solutions, sodium nitrate has a greater influence than potassium nitrate. Unfortunately, this point cannot be further tested in the meantime, since his data, otherwise much more comprehensive and numerous than ours, do not include numbers for sodium bromide or sodium iodide. That this close similarity should be found in the case of two substances like *l*-malic acid and ethyl *d*-tartrate, which we think would not generally have been expected to behave quite analogously, is certainly very noteworthy. The influence of the salts is, it will be observed, of an exactly similar character, depressing the rotation of the ethyl *d*-tartrate and raising that of *l*-malic acid. They would thus act in the same sense on the substances of corresponding configuration, ethyl *d*-tartrate and *d*-malic acid.

Most of the salts dealt with above were examined only at one concentration, and in most cases it would not be possible to investigate their effects over any great range of concentration. We examined sodium chlorate, however, as one of the most soluble, up to a strength of $6N$. The results are given in the table below, along with an observation on potassium chlorate already referred to.

TABLE III.

Salt.	Approximate strength of aqueous solution.	Percentage of salt in total solution.	p.	α_D^{26}.	Depression of α_D^{26}.	$d_{4^\circ}^{20^\circ}$.	$[\alpha]_D^{26}$.	Depression of $[\alpha]_D^{26}$.
$KClO_3$...	$2/5N$	4·199	10·14	+2·57°	0·28°	1·047	+24·21°	2·16°
$NaClO_3$.	$2/5N$	3·665	10·20	2·60	0·25	1·045	24·40	1·97
$NaClO_3$.	$2N$	16·00	8·89	1·89	0·96	1·132	18·78	7·59
$NaClO_3$.	$4N$	27·67	7·66	1·32	1·53	1·227	13·96	12·41
$NaClO_3$.	$6N$	36·42	6·73	0·79	2·06	1·308	8·976	17·394

In order to explain clearly the meaning of the various columns of the table, it will be sufficient to say that the last solution consisted of 50 c.c. of water, to which were added 32·038 grams of sodium chlorate, giving an approximately $6N$-solution. To this was then added 5·92 grams of ethyl tartrate, so that the mixed solution contained 32·038 grams of salt in a total weight of $32·038 + 50 + 5·92 = 87·958$ grams, or 36·42 per cent. Similarly, the solution contained 5·92 grams of ethyl tartrate in 87·958 grams of solution, or $p = 6·73$.

It will be observed that the effect of the sodium chlorate increases regularly, but not quite linearly, as its quantity in the solution becomes greater; the curve obtained by plotting specific rotation against concentration is, in fact, very similar indeed to those given by Stubbs (*loc. cit.*, p. 2270) to illustrate his results.

In $6N$-solution sodium chlorate reduces the specific rotation of the dissolved ethyl tartrate by over 17°, and in this connexion we may refer to the idea which has been put forward repeatedly in recent years by various chemists, namely, that a salt when dissolved in water combines with and renders inactive part of the solvent. The idea has been applied by H. E. Armstrong in a number of different ways; it was applied by Philip (Trans., 1907, **91**, 711) in regard to the influence of non-electrolytes and electrolytes on the solubility of sparingly soluble gases in water, and, in fact, the suggestion of solvation has become a simple and fairly generally recognised method of escape from theoretical difficulties of all sorts. The idea, so far as the results of Philip are concerned, has been criticised by Usher (Trans., 1910, **97**, 66), who points out that it involves three assumptions: (1) That hydrates are formed; (2) that the gas is insoluble in the dissolved substance; and (3) that it is insoluble in the hydrate. It has also been referred to by Stubbs (*loc. cit.*, pp. 2281, 2282), who rejects the suggestion entirely, on the ground that the influence in the case of barium chloride, for example, is several times greater than would be produced by complete dehydration of the malic acid, and also that, in general, salts with the greatest affinity for water, like lithium chloride, have, in fact, the least effect.

Our results strongly support this conclusion. The specific rotation of ethyl tartrate at 26° is +8·47°, and that of the solution we have examined, namely, 5·92 grams of ester in 50 c.c. of water, is +26·37°, the rise due to solution in water being thus 17·9°. From the data given above for the influence of sodium chlorate, it appears that this rise would be completely neutralised by the addition of sufficient sodium chlorate to form with the water a $6·3N$-solution. There is, however, absolutely nothing to indicate that the addition of sodium chlorate beyond this amount would not continue to influence the rotation in much the same manner as before.

The same conclusion can be deduced from the behaviour of solutions containing barium chloride. One thirtieth part of a gram-molecular weight of this salt produces a greater effect (+12·43°, table I) than one-tenth of a gram-molecular weight of any other of the salts examined, and in this, again, is evident the strong resemblance between our results and those of Stubbs, who also found barium chloride to have a very powerful influence.

Stubbs (*loc. cit.*, p. 2282), after considering various theories, puts forward the rather vague proposition, "that the influence is mainly due to a direct and distinctive power possessed by the inactive molecules in solution to affect the asymmetry of the active ones within their sphere of influence without actual chemical combination," and for four reasons, namely, (i) the additive nature of the effect of strong positive and negative radicles, (ii) the smallness of the effect of mercuric chloride and acetic acid, (iii) the parallelism between low influence and low conductivity in the case of barium nitrate, and (iv) the consideration that most of the properties of solutions of electrolytes are actually ionic, he considers it "reasonable to conclude that the large effects tabulated . . . are chiefly produced by the ions."

Now if this were the case, it might perhaps be expected that in an ethyl tartrate solution ionisation would be less than in one of malic acid, and therefore that the effects observed by us would be smaller than those found by Stubbs, instead of being in reality much greater, and, further, the attempt to connect the phenomena under discussion with ionisation appears rather to ignore the possibility of an action on the active compound of the inorganic salt as a whole. The nature of any such action could, of course, not be investigated by Stubbs or others working with a solid active substance, but in the case of a liquid like ethyl tartrate the question can be examined, and we therefore extended our experiments to the influence of inorganic salts on homogeneous ethyl tartrate, although most inorganic salts are only sparingly soluble in the ester.

In our experiments the various salts used were weighed out into a flask. Ten c.c. of ethyl tartrate were then added from a pipette, and the weight of the ester was adjusted to 11·974 grams in each case, which can easily be done without interfering with the salt in any way. The mixture was then slightly heated until the salt dissolved, after which the rotation was determined at 26°. The results are given in table IV.

TABLE IV.

Effect on the Rotation of Homogeneous Ethyl Tartrate (α_D^{26} 10·2°) *of the Addition of Various Substances.*

Added substance.	M.W.	Weight of substance in 100 grams of solution (grams).	Weight of substance added to 100 grams of ethyl tartrate (milligram-molecular weights).	Depression of $\alpha_D^{26°}$.
Thiocarbamide	76	0·1667	2·198	0·21°
		0·5812	7·692	0·63
		1·392	18·574	0·87
		1·643	21·98	0·95
Mercuric chloride	271	0·8282	3·082	1·08
		1·657	6·164	1·48
		4·142	15·400	2·14
		5·896	23·11	2·68
Mercuric iodide	454	0·8282	1·84	0·45
Sodium acetate	82	6·000	77·86	7·112
Potassium bromide	119	0·1675	1·404	0·53
		0·4158	3·510	1·92
		0·8283	7·019	2·56
		0·9821	8·335	2·44
Sodium bromide	103	0·4158	4·054	1·16
		0·8283	8·11	2·55
Sodium iodide	150	0·8283	5·568	2·38

Barium chloride was too sparingly soluble to be examined.

These inorganic salts have, clearly, much the same effect on the rotation of homogeneous ethyl tartrate as they have on that of its aqueous solutions. The depression is very rapid and very considerable for sodium bromide, sodium iodide, and potassium bromide, addition of about 1 per cent. of the last-named producing a depression of about 24 per cent. in the rotation. The influence is less marked for sodium acetate and mercuric chloride (again in agreement with the results of Stubbs), and still less for thiocarbamide. Of organic solvents hitherto examined, acetylene tetrabromide was one of the most powerful in depressing the rotation of the ester, but it is not so powerful as thiocarbamide. The difference between the solvent influence of an inorganic substance and an organic substance as a solvent seems to be merely one of degree, and so far as these results go it seems improbable that ionisation plays any important part in the matter, especially since the regularities which appear in table II for the aqueous solutions occur also, although from the nature of the case, not quite so obviously, for the homogeneous ester; thus, in equivalent concentration, potassium bromide (8·335 milligram-molecules, Δ = 2·44°) and sodium bromide (8·11 milligram molecules, Δ = 2·55°) have much the same effect, whilst sodium iodide (5·568 milligram-molecules, Δ = 2·38°) has a much greater influence than sodium bromide (4·054 milligram-molecules, $\Delta = 1{\cdot}16^\circ$), but considering the sparing solubility of most of these salts in ethyl tartrate, too much stress ought not to be laid on this.

Finally, the above results may be compared with one recorded by Walden (*Ber.*, 1905, **38**, 407), who found that ethyl tartrate, the rotation of which was $\alpha_D^{15} + 6{\cdot}1^\circ$, gave, after saturation with hydrogen bromide (the solution containing about 10 per cent. of the latter), $\alpha_D^{15} - 7{\cdot}0^\circ$, a change of rotation of over 13°. The most soluble of the salts we have examined, sodium acetate, gave a depression of 7·1° in a solution containing 6 per cent. of it by weight, and since sodium bromide and potassium bromide are much more powerful than sodium acetate, it would seem that they resemble hydrogen bromide closely in their influence. The large effect of hydrogen bromide is regarded by Walden as strong evidence in favour of combination of the acid with the ester, in which case it would be necessary to assume a similar combination for the inorganic salts. There is, however, nothing to show that the influence of inorganic salts is of a different order from that of organic solvents, and as no evidence of any weight has hitherto been brought forward in favour of combination in the latter, better investigated case, there seems to be no valid reason for assuming it in the former either.

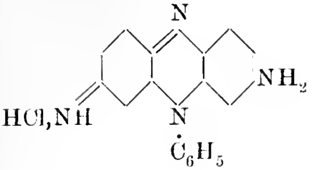
We had intended this research to be more extensive, but the entry of one of us on other duties rendered this impossible for the present. The polarimetric measurements recorded in the paper were carried out by means of an instrument placed at our disposal by the Carnegie Trustees for the Universities of Scotland, to whom we have pleasure in expressing our thanks.

Organic Chemistry Department,
University of Glasgow.

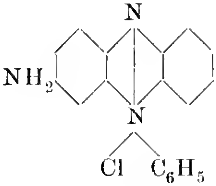
CXCV.—*Studies in the Azine Series. Part II.*

By Kathleen Balls, John Theodore Hewitt, and Sidney Herbert Newman.

Some years ago one of the present authors suggested that the fluorescence of safranine and its symmetrical derivatives might be explained by a double tautomerism (*Zeitsch. physikal. Chem.*, 1900, **34**, 15), which can be expressed by the scheme:



(I.)



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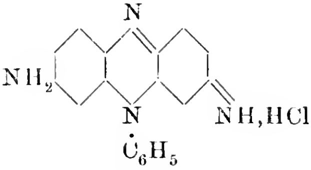
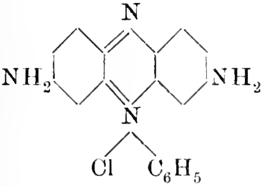


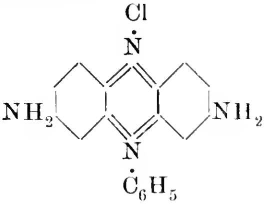
(III.)

The symmetrical formula (II) might be written with an orthoquinonoid structure; in fact, the constitutions



(IV.)

and



(V.)

have been suggested respectively by Kehrmann (*Ber.*, 1899, **32**, 2601) and Green (*Rev. Gén. Mat. Col.*, 1897, **1**, 269; *Ber.*, 1899, **32**, 3155).* Kehrmann has consistently assumed the correctness of the constitution he has given, apparently regarding the chief argument in its favour as the possibility of displacing both amino-groups by hydrogen, and so arriving at salts of phenylphenazonium (*Ber.*, 1896, **29**, 2316). It should be noted, however, that in acid of medium concentration only one amino-group is diazotised; if the resulting monodiazonium salt is boiled with alcohol, *apo*safranine (monoaminophenylphenazonium chloride) results. To remove the second amino-group, diazotisation in concentrated acid solution must be resorted to, and since safranine behaves as a mono-, di-, or tri-acidic base according to the concentration of the acid used to form the salt, arguments based on the diazotisability of an amino-group when dissolved in concentrated acid by no means prove that the amino-group is also present in the mon-acid salt. Jaubert

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* Formulæ are employed in this paper with a diagonal linking. This is understood as equivalent to an orthoquinonoid structure and not opposed to it. It has been used on account of symmetry, to avoid discussion as to which half of the molecule happens to be quinonoid at a particular instant.

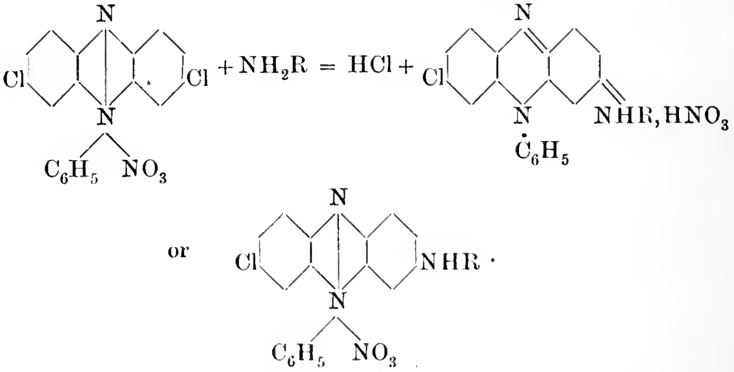
(*Ber.*, 1895, **28**, 510, 1584) measured the amount of nitrite used when phenosafranine was diazotised, and found it was only one molecular proportion. This was considered by him to be an argument for an asymmetric constitution (I or III), but it hardly excludes the possibility of tautomerism with a structure as represented by II, IV, or V.

In the circumstances, further experimental evidence to show that the molecule does not contain two free amino-groups at the same instant appeared desirable, although completely to prove the symmetrical tautomerism it should be demonstrated that either one or other of the amino-groups might be the one entering into reaction.

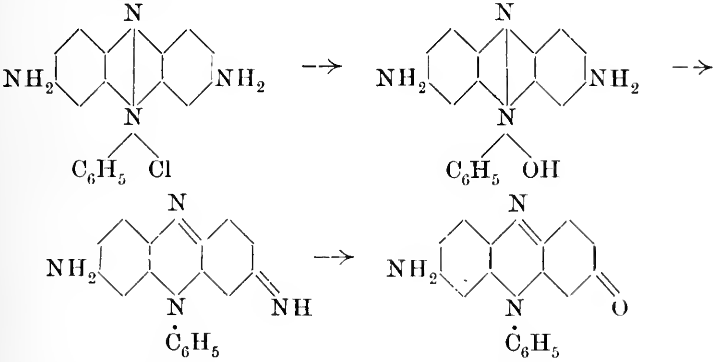
In the experimental part of the paper details are given as to methods by which the problem can be attacked; the position we assign to the amino-groups (actual or potential) is that given by Bernthsen rather than by Witt; the evidence which has been accumulated appears to us unanswerable (Trans., 1909, **95**, 577). The following arguments may be brought forward in favour of a continuous or intermittent para-quinonoid structure of the molecule.

The phenylphenazonium compounds which are structurally incapable of assuming a para-quinonoid configuration are very unstable; they react readily with numerous substances in such a way as to form compounds which are capable of assuming a para-quinonoid as well as an ortho-quinonoid form; once such a compound has been produced, the excessive reactivity disappears. This may be illustrated by the following examples:

(i) Dichlorophenylphenazonium salts react immediately with bases in the cold, one chlorine atom being displaced:



To displace the second chlorine atom, strong heating with excess of base has to be resorted to. Moreover, the remaining chlorine atom is not displaced by hydroxyl, even by prolonged boiling with equal volumes of 50 per cent. potassium hydroxide and alcohol, or by heating in sealed tubes with the same mixture to 150°. The result is comparable with the behaviour of phenosafranine, which has an amino-group displaced by hydroxyl (or imino-group by oxygen) when heated with aqueous sodium acetate to 150° (O. Fischer and E. Hepp, *Ber.*, 1897, **30**, 399); the resulting safraninone (aminosafranone) is a stable substance, and in order to convert phenosafranine into hydroxy*apo*safranone very prolonged boiling with alcoholic potassium hydroxide must be resorted to. Such behaviour appears to be in accordance with the scheme:

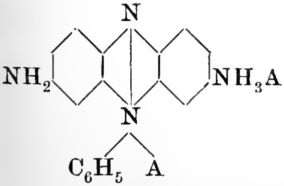


Unstable. Stable.

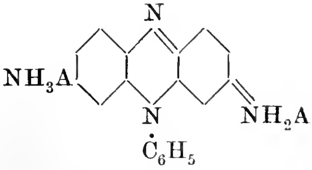
(ii) In the safranines, that is, diamino-substituted phenylphenazonium compounds, no distinction can be drawn between the two amino-groups provided they are unsubstituted or have hydrogen atoms replaced by identical radicles; nevertheless, if one amino-group is attacked, the other ceases to exercise the functions of an amino-group.

(*a*) Attention has been drawn to the impossibility of diazotising both amino-groups at the same time in solution of acid of medium concentration; the existence of two groups $\cdot NH_3A$ (A = acid radicle) simultaneously in the molecule appears only to happen for the tri-acid salts. Tautomeric formulæ in equilibrium have already been suggested for the mon-acid salts; the di-acid and tri-acid salts probably have constitutions given by the following or similar formulæ:

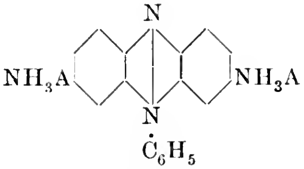
Di-acid:



and



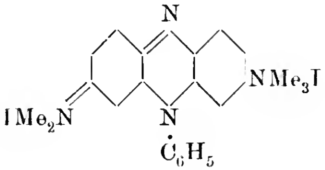
Tri-acid:



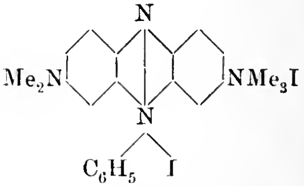
It will be noticed that with either formula only one diazotisable $\cdot NH_3A$ group exists in the di-acid salts.

(*b*) Phenosafranine (mon-acid salts) reacts with one molecule of an aldehyde; if its constitution were such that its molecule always contained two free amino-groups, it should react with 2 molecules.

(*c*) The iodide of tetramethylphenosafranine combines with only 1 molecule of methyl iodide; to the resulting methiodide one must ascribe the two structures:



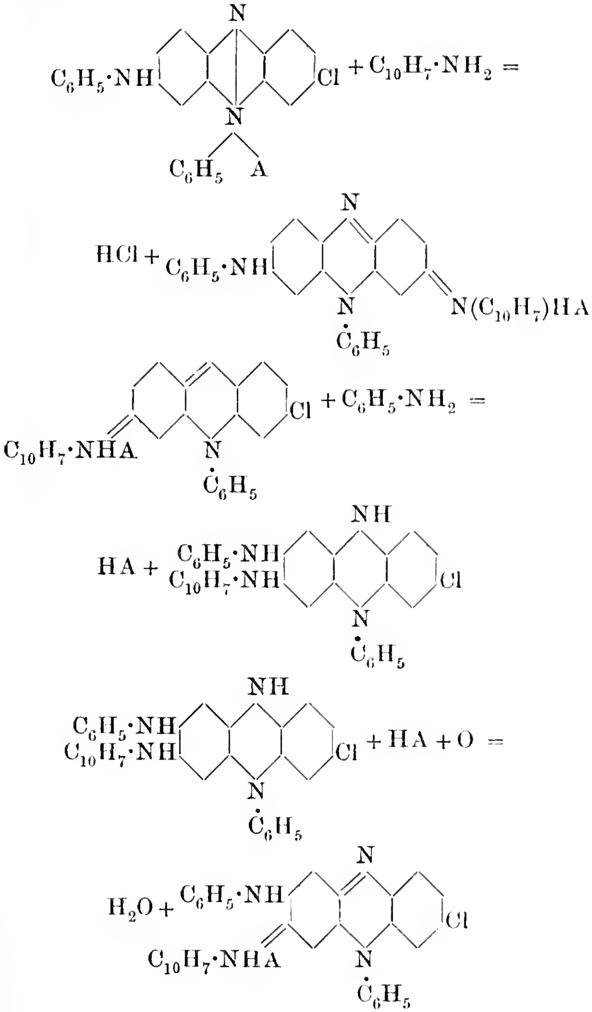
and



for were it represented exclusively by the latter formula, no reason exists why another molecule of methyl iodide should not be added on by the free dimethylamino-group.

An attempt was made to prove the equivalence of position of the two chlorine atoms in dichlorophenylphenazonium salts by their successive replacements with two distinct arylamino-groups. Dichlorophenylphenazonium nitrate reacted with aniline in the cold to give phenylaminochlorophenylphenazonium nitrate; the second chlorine atom was replaced by an α-naphthylamino-group by fusion with α-naphthylamine. If, however, an α-naphthylaminochlorophenylphenazonium salt is heated with aniline, although a phenylamino-group is introduced into the molecule, the chlorine atom is not eliminated. The different behaviour of the phenylamino- and naphthylamino-compounds finds its simplest explanation in assigning to the latter a para-quinonoid constitution; the aniline then adds itself to the quinonoid substance, and the leuco-compound formed undergoes oxidation (p. 1845).

Although the intended proof of equivalence of chlorine position could not be furnished, the result affords welcome support to the view of the almost complete balance between ortho- and para-quinonoid structure, which may be displaced in one direction or the other according to the nature of the substituent group.

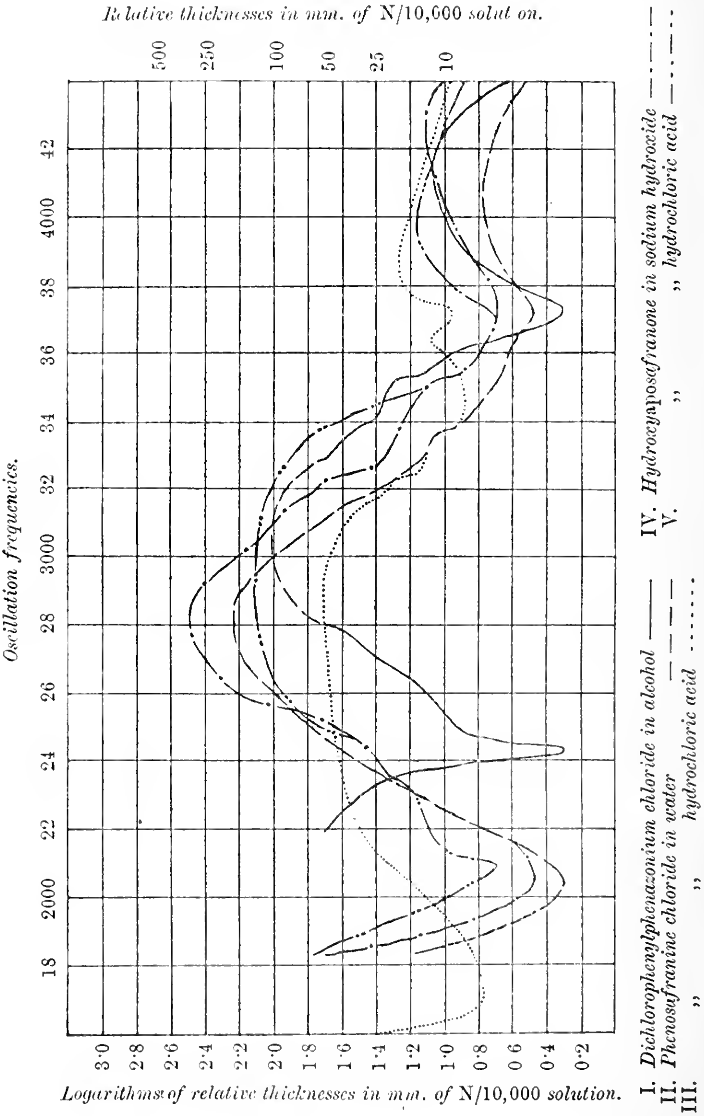


EXPERIMENTAL.

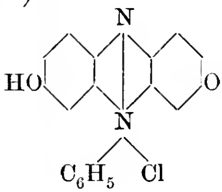
*Hydroxy*apo*safranone*.—This substance was prepared by Jaubert's process, and purified by the method already described (Trans., 1909, **95**, 580). Since the substance can act either as weak acid or weak base, its absorption spectra in alkaline and acid solutions were measured. In Fig. 1 it will be noticed that the alkaline solution gives a broad band with head at an oscillation frequency of about 2050, and in some ways resembling a band given by the mon-acid salts of phenosafranine. When hydroxy*apo*-

safranone is dissolved in concentrated hydrochloric acid, a narrower band is produced in the visible spectrum, but the oscillation

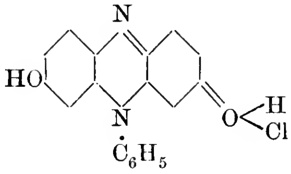
FIG. 1.



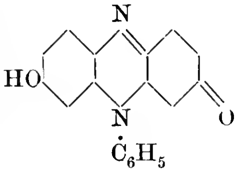
frequency of its head is not far removed from that of the band produced by an alkaline solution. The shape of the band as plotted reminds one to some extent of the band of dichlorophenylphenazonium chloride. We had expected the correspondence, not only in shape, but also position, to be a very close one, as we looked on the hydrochloride of hydroxy*apo*safranone as being really dihydroxyphenylphenazonium chloride (I); possibly, however, the salt is not an ortho-quinonoid ammonium, but a para-quinonoid oxonium salt (II):



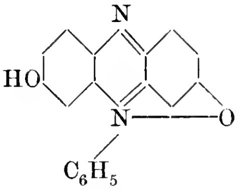
(I.)



(II.)



(III.)



(IV.)

Meanwhile, we agree with Decker in strongly preferring formula III as advocated by Jaubert to Kehrmann's formula IV for hydroxy*apo*safranone and its salts with bases. Formula IV, which represents the substance as a phenolbetaine of a quaternary ammonium compound, should imply strongly basic properties. As a matter of fact, the hydrochloride of hydroxy*apo*safranone is immediately hydrolysed by water, whereas phenylphenazonium chloride is a stable neutral salt. A specific negative influence of the hydroxyl group cannot be argued, as the hydroxyphenyltrimethylammonium hydroxides are practically as basic as the parent phenyltrimethylammonium base.

Safranine.—The similarity of the absorption spectra of alkaline hydroxy*apo*safranone and of the mon-acid salt of phenosafranine points to a considerable proportion of the latter existing in solution in a para-quinonoid condition. In Fig. 1 the absorption of the di-acid salt obtained by dissolving phenosafranine in equal volumes of water and fuming hydrochloric acid is given. Presumably a salt formed with two molecules of acid should exhibit less residual affinity than a mon-acid salt; nevertheless, the absorption is in this case displaced towards the red end of the spectrum.

Condensation Product of Safranine and Benzaldehyde.—Phenosafranine chloride was dissolved in ten times its weight of boiling water, one molecular proportion of benzaldehyde added, the whole well shaken, and allowed to remain overnight. The contents of the flask had set to a nearly solid mass, the product was collected, washed with alcohol, ground finely, washed with 50 per cent. alcohol, and dried for some days on porous earthenware over sulphuric acid:

0·2673 gave 0·0890 AgCl. Cl = 8·24.
0·1207 „ 15·15 c.c. N_2 at 22° and 740 mm. N = 14·03.
0·1276 „ 14·6 c.c. N_2 at 14° and 760 mm. N = 13·57.
$C_{25}H_{19}N_4Cl$ requires Cl = 8·63; N = 13·67 per cent.

The same substance was obtained from 1 gram of phenosafranine chloride and 0·69 gram (2 molecules) of benzaldehyde by boiling with 50 per cent. alcohol, keeping overnight, collection, and recrystallisation from 50 per cent. alcohol; thus, phenosafranine is seen to react with only 1 molecule of benzaldehyde.

Condensation Product with p-*Hydroxybenzaldehyde.*—Prepared in a similar manner by mixing hot aqueous solutions of the components. The crystals separating on cooling were collected, washed with small quantities of cold water, and dried:

0·1373 gave 14·85 c.c. N_2 at 7° and 757 mm. N = 13·17.
$C_{25}H_{19}ON_4Cl$ requires N = 13·13 per cent.

Tetramethylphenosafranine.—Several salts have been prepared by Bindschedler (*Ber.*, 1883, **16**, 867). We obtained our material by reducing 15 grams of nitrosodimethylaniline hydrochloride in 160 grams of 50 per cent. acetic acid with zinc dust (about 16 grams) until colourless, then adding 10 grams of dimethylaniline, a few c.c. of glacial acetic acid in order to give a clear solution, and subsequently 13·5 grams of ammonium dichromate in 30 c.c. water. After remaining half-an-hour for completion of indamine formation, 7·5 grams of aniline were added; after a further half-hour, 13·5 grams of ammonium dichromate in 30 c.c. water were added, and safranine formation completed by gently boiling for one hour. The hot solution was filtered, the residue repeatedly extracted with boiling water, and the united filtrates salted out. The colouring matter was recrystallised from boiling water with addition of a few drops of hydrochloric acid:

0·1884 gave 0·0701 AgCl. Cl = 9·20.
$C_{22}H_{23}N_4Cl$ requires Cl = 9·36 per cent.

The *iodide* separates in fine needles on adding potassium iodide solution to a hot solution of the chloride and allowing to cool:

0·2396 gave 0·1286 AgI. I = 29·02.
0·1203 „ 0·0653 AgI. I = 29·03.
$C_{22}H_{23}N_4I$ requires I = 27·02 per cent.

We are unable to account for the high value for iodine; the two analyses were carried out by different persons (S.H.N. and J.T.H.) on different preparations.

Tetramethylphenosafranine iodide methiodide was obtained in a fairly pure condition by heating the iodide with a slight excess of methyl iodide for three hours at 100°. The product was collected, washed successively with small quantities of water and alcohol, and dried:

0·1932 gave 0·1455 AgI. I=40·71.
$C_{23}H_{26}N_4I_2$ requires I=41·49 per cent.

Dichlorophenylphenazonium Salts.—In our earlier experiments dichlorophenylphenazonium chloride prepared from synthetic hydroxy*apo*safranone by O. Fischer and Hepp's method (*Ber.*, 1898, **31**, 301) was employed. As these authors analysed the nitrate, we checked the purity of our specimen:

0·1160 gave 0·1309 AgCl. Cl=29·23.
$C_{18}H_{11}N_2Cl_3$ requires Cl=29·44 per cent.

The more sparingly soluble nitrate is, according to Fischer and Hepp, more easily obtained in a pure condition; this we quite confirm, and subsequently we used this salt exclusively. We modified Fischer and Hepp's method, which consists in suspending hydroxy*apo*safranone in phosphoryl chloride, and then adding phosphorus pentachloride, since we found that the quality of the phosphoryl chloride greatly influenced the yield. A mixture of 8 grams of phosphorus pentachloride and 2 grams of phosphoric oxide is warmed for twenty minutes in a beaker, then cooled; 6 grams of hydroxy*apo*safranone are added, the whole well mixed, and after ten minutes a further 8 grams of phosphorus pentachloride is added, and the mixture heated on the water-bath for fifteen minutes. After cooling, the fusion is poured into anhydrous ether, the yellow precipitate collected, washed with ether, dissolved in hot water, and the nitrate salted out by addition of potassium nitrate. The absorption spectrum of the chloride is given in Fig. 1.

Phenylaminochlorophenylphenazonium Salts.—As stated by Fischer and Hepp (*loc. cit.*, p. 302), the chloride is produced by the interaction of aniline and dichlorophenylphenazonium chloride in the cold. We checked the purity of our specimen analytically after crystallisation from alcohol. (Found, Cl=17·26; $C_{24}H_{17}N_3Cl_2$ requires Cl=17·0 per cent.)

The *nitrate* was obtained by suspending 1·4 grams of dichlorophenylphenazonium nitrate in about 10 c.c. of alcohol, and gradually adding 0·7 c.c. of aniline. 0·9 Gram of salt separated in a crystalline condition; it was recrystallised by addition of petroleum to its solution in nitrobenzene, when very small, obliquely terminated prisms were obtained; from alcohol the salt separates in interlaced needles:

0·1210 gave 0·2858 CO_2 and 0·0498 H_2O. C=64·79; H=4·03.
0·1084 „ 11·8 c.c. N_2 at 13·5° and 778 mm. N=12·88.
0·1110 „ 0·0360 AgCl. Cl=8·03.
$C_{24}H_{17}O_3N_4Cl$ requires C=64·55; H=3·80; N=12·60; Cl=7·99 per cent.

Phenylaminonaphthylaminophenylphenazonium Nitrate.—2·51 Grams of phenylaminochlorophenylphenazonium nitrate were gradually added to 1·44 grams of molten α-naphthylamine. The mass was maintained in a molten condition for five minutes, and continually stirred, then cooled, extracted with alcohol, and filtered into dilute nitric acid. The precipitate was collected, again dissolved in alcohol, and reprecipitated with dilute nitric acid, boiled with excess of dilute nitric acid, and collected. The salt separates from alcohol as a fine, crystalline powder with a bronze reflex; the alcoholic solution is deep blue with a violet tinge when viewed by transmitted light:

0·1411 gave 0·3802 CO_2 and 0·0578 H_2O. C=73·6; H=4·5.
0·1356 „ 14·4 c.c. N_2 at 14° and 759 mm. N=12·6.
$C_{34}H_{25}O_3N_5$ requires C=74·0; H=4·5; N=12·7 per cent.

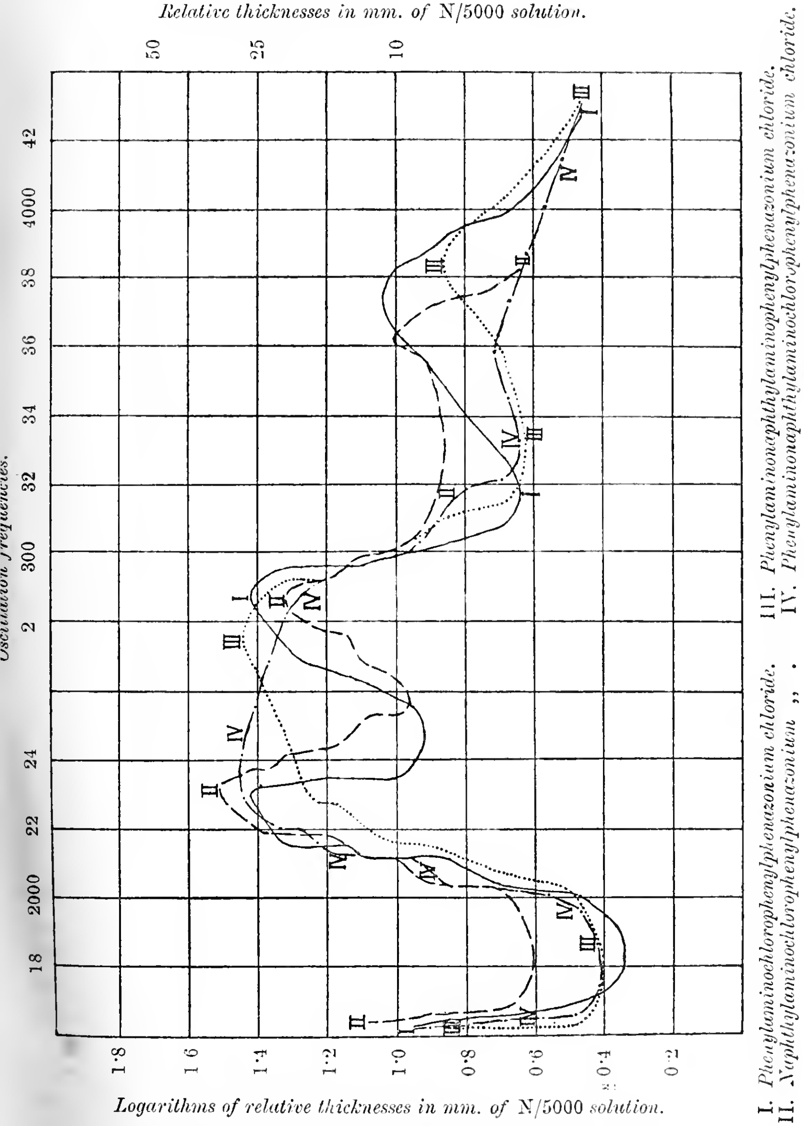
α-Naphthylaminochlorophenylphenazonium Nitrate.—A suspension of 3 grams of dichlorophenylphenazonium nitrate in alcohol was treated with an alcoholic solution of 2·3 grams of α-naphthylamine; after some time the solution was gently warmed, and poured into an excess of dilute nitric acid. The treatment was repeated, and the purple, crystalline precipitate was collected and dried:

0·1160 gave 0·2880 CO_2 and 0·0325 H_2O. C=67·8; H=3·1.
0·1310 „ 12·7 c.c. N_2 at 17° and 751 mm. N=11·3.
0·1192 „ 0·0452 AgCl. Cl=7·4.
$C_{28}H_{19}O_3N_4Cl$ requires C=68·0; H=3·8; N=11·3; Cl=7·2 per cent.

The solution in alcohol is purple, and appears of a redder shade than the corresponding anilino-compound. Usually naphthylamino-compounds are bluer in shade than the corresponding substances containing phenylamino-groups; in this case, however, the band is less persistent (see Fig. 2, scale different from that of Fig. 1), and is not displaced as much as might have been expected towards the red end of the spectrum. Possibly, as has been mentioned above, the phenyl- and naphthyl-amino-compounds possess different constitutions.

Phenylamino-α-naphthylaminochlorophenylphenazonium Nitrate.—Two grams of naphthylaminochlorophenylphenazonium chloride were added gradually to 2 c.c. of boiling aniline; the mixture was gently heated for ten minutes, poured into concentrated hydrochloric acid. The precipitate was collected, and the salt converted

FIG. 2.



into nitrate by twice dissolving it in hot alcohol and pouring into excess of dilute nitric acid. The nitrate separates from alcohol as a crystalline powder; the solution is bluer than that of the naphthylaminochloro-compound from which it is obtained:

0·0970 gave 0·2482 CO_2 and 0·0388 H_2O. C = 69·9; H = 4·5.
0·1086 „ 0·2796 CO_2 „ 0·0450 H_2O. C = 70·1; H = 4·4.
0·1008 „ 10·4 c.c. N_2 at 21° and 763 mm. N = 11·8.
0·1328 „ 0·0324 AgCl. Cl = 6·0.

$C_{31}H_{24}O_3N_5Cl$ requires C = 69·8; H = 4·1; N = 11·9; Cl = 6·0 per cent.

The absorption spectrum of this compound has also been measured, and will be found in Fig. 2.

In conclusion, the authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant, by which the expenses of this investigation have been defrayed.

EAST LONDON COLLEGE,
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CXCVI.—*The Action of Halogens on Silver Salts and on Potassium Cyanate in Presence of Water, with a Note on the Decomposition of Cyanic Acid in Aqueous Solution.*

By CHARLES WILLIAM BLYTH NORMAND and ALEXANDER CHARLES CUMMING.

SOME time ago it was noticed that when iodine and silver cyanate were mixed with water, interaction occurred with the formation of silver iodide. The only soluble product appeared to be carbamide.

This seemed sufficiently interesting to warrant further investigation, as the formation of carbamide was scarcely to be expected from such a reaction, whilst examination of the literature threw no light on the subject. The only researches of a systematic nature on the action of halogens on silver salts seem to be those of Birnbaum and collaborators (*Annalen*, 1869, **152**, 111; also Berl, *Ber.*, 1880, **13**, 1270; 1882, **15**, 456), but in these researches it is mainly the action of dry iodine on dry silver salts of organic acids that has been studied.

For convenience the present communication has been confined to reactions in the presence of water, since it was found that the reactions occurred in wholly different ways according to whether water was present or not.

Reactions in Presence of Water.

It was shown by Jakowkin (*Zeitsch. physikal. Chem.*, 1899, **29**, 656) that chlorine is considerably hydrolysed in aqueous solution, according to the equation:

$$Cl_2 + H_2O = H^{\cdot} + Cl' + HClO.$$

Hydrolysis of a similar type has been shown to occur with bromine solutions (Jakowkin, *ibid.*, 1912, **70**, 188; Bray, *J. Amer. Chem. Soc.*, 1910, **32**, 932; Bray and Connolly, *ibid.*, 1911, **33**, 1485). Bray has shown from his own results and those of Sammet (*Zeitsch. physikal. Chem.*, 1905, **53**, 687) that in aqueous iodine solution both of the following reactions occur to an appreciable extent:

$$(1)\quad I_2 + H_2O = H^{\cdot} + I' + HIO.$$
$$(2)\quad 3I_2 + 3H_2O = 6H^{\cdot} + 5I' + IO'_3.$$

The concentrations of the substances present in saturated aqueous solutions of the halogens at 25° are as follows (gram-molecules per litre):

Cl_2 = about 0·13 Cl' = about 0·036
Br_2 = 0·21 $Br' = 0{\cdot}37 \times 10^{-3}$ $HBrO = 1{\cdot}71 \times 10^{-3}$
I = 0·00132 I' = less than $4{\cdot}0 \times 10^{-5}$ HIO = less than $4{\cdot}0 \times 10^{-6}$

The IO'_3 concentration, when the solution has attained equilibrium according to the second equation given above, is $0{\cdot}53 \times 10^{-5}$. Solubility data (Landolt-Börnstein, "Tabellen," 1905) show that the solubility products at 20° for silver halides are:

$$(Ag^{\cdot})(Cl) = 1 \times 10^{-10}, \qquad (Ag^{\cdot})(Br) = 2{\cdot}5 \times 10^{-14},$$
$$(Ag^{\cdot})(I) = 2 \times 10^{-16}.$$

Even with chlorine, therefore, it is only necessary that the silver ion concentration should reach 3×10^{-9} for interaction to occur with precipitation of silver chloride. The only compound with which we experimented in which the concentration probably does not reach this value was silver acetylide. Silver thiocyanate was the least soluble salt of an ordinary type, and it has a solubility at 20° of $8{\cdot}3 \times 10^{-7}$ gram-equivalents per litre (Böttger, *Zeitsch. physikal. Chem.*, 1903, **46**, 602).

EXPERIMENTAL.

Silver Acetate and Iodine.—When a solution of silver acetate is treated with iodine, a reaction takes place immediately. If the amounts taken are in the ratio of one atom of iodine to one molecule of silver acetate, the products are silver iodide, silver iodate, and acetic acid. Birnbaum (*loc. cit.*) found that the reaction occurred according to the equation:

$$(3)\quad 6C_2H_3O_2Ag + 3H_2O + 3I_2 = 5AgI + AgIO_3 + 6C_2H_4O_2.$$

We arrived at the same conclusion before finding a reference to Birnbaum's paper. We found, further, that the reaction was accurately quantitative if the silver acetate and iodine are heated with water.

If excess of iodine was added, silver iodate was no longer found in the precipitate, but the filtrate contained iodic acid in addition to acetic acid. This reaction is represented by the equation:

$$(4)\quad 5C_2H_3O_2Ag + 3H_2O + 3I_2 = 5AgI + 5C_2H_4O_2 + HIO_3.$$

On the assumption that the reaction occurs between the highly ionised silver acetate and the hydrolysis products of iodine, a simple representation of these reactions is obtained. Reaction 4 then becomes:

$$5Ag^{\cdot} + 5(C_2H_3O_2)' + 3H^{\cdot} + 2I' + IO'_3 = 5AgI + 5C_2H_4O_2 + H^{\cdot} + IO'_3,$$

whilst addition of an additional equivalent of silver acetate (Reaction 3) leads to the precipitation of silver iodate:

$$H^{\cdot} + IO'_3 + Ag^{\cdot} + (C_2H_3O_2)' = AgIO_3 + C_2H_4O_2.$$

It cannot, however, be definitely stated that this is the actual course of the reaction. A satisfactory representation is also obtained by assuming that the first reaction is that given by equation 3, and that the silver iodate then reacts with more iodine according to the equation (Naquet, *Jahresber.*, 1860, 201):

$$5AgIO_3 + 3H_2O + 3I_2 = 5AgI + 6HIO_3.$$

Silver Sulphate and Bromine.—Water was added to a weighed amount of silver sulphate, and bromine was aspirated through this mixture until the water remained permanently coloured with the bromine. The precipitate formed consisted of silver bromide, and the solution contained sulphuric acid and either hypobromous or bromic acid, according to the temperature at which the experiment was conducted. The main reaction, if the solution was kept near 0°, led to the formation of hypobromous acid, according to the equation:

$$Ag_2SO_4 + 2Br_2 + 2H_2O = 2AgBr + 2H_2SO_4 + 2HBrO.$$

If the solution was heated, bromic acid was obtained instead of hypobromous acid:

$$5Ag_2SO_4 + 6Br_2 + 6H_2O = 10AgBr + 5H_2SO_4 + 2HBrO_3.$$

The weight of silver bromide obtained was slightly lower than that calculated, possibly because some of the silver sulphate particles became coated with silver bromide, and thus prevented further action. Dancer (*Journ. Chem. Soc.*, 1862, **15**, 477) utilised the similar action of bromine on silver nitrate as a mode of preparing hypobromous acid.

It was mentioned in the introduction that iodine in aqueous solution is hydrolysed in two ways, and in pure water yields both hypoiodous acid and iodate ions. Reactions with iodine therefore usually result in the formation of an iodate. With chlorine and bromine solutions there appears to be little, if any, tendency to form chlorate and bromate by hydrolysis at the ordinary temperature, and reactions with chlorine and bromine therefore yield hypochlorous or hypobromous acids. The formation of bromic acid when bromine and silver sulphate react in hot solution may be due to appreciable hydrolysis of bromine according to the equation:

$$3Br_2 + 3H_2O = 6H^{\cdot} + 5Br' + BrO'_3.$$

It may, however, be equally well accounted for by secondary decomposition of hypobromous acid:

$$3HBrO = 3H^{\cdot} + 2Br' + BrO'_3.$$

When the current of bromine was stopped before all the silver sulphate was decomposed, the solution, after being filtered from silver bromide and bromate, possessed certain properties which indicated the presence of a small amount of a hypobromite and of a silver salt. It seemed possible that the silver salt was silver hypobromite, but as the alleged existence of this salt rests on some rather inconclusive experiments of Balard (*J. pr. Chem.*, 1835, **4**, 179), attempts were made to prepare it from silver oxide and bromine, according to Balard's method.

Silver Oxide and Bromine.

Non-existence of Silver Hypobromite.—Silver oxide, which had been freshly precipitated and well washed, was added to water, and bromine vapour was aspirated through the mixture, which was kept cold by being surrounded by ice. The bromine was immediately decolorised, and silver bromide formed. The action was always stopped before all the silver oxide was decomposed. After filtering, the precipitate was found to be a mixture of the bromide, bromate, and oxide of silver. The presence of silver bromate was proved by shaking the precipitate with a potassium bromide solution and then acidifying. The liberation of bromine showed that bromate was present.

The filtrate had an odour similar to that of bleaching solution, and it decolorised indigo. On account of this oxidising action, it was not possible to determine by means of the ordinary indicators if the solution was acid. Without being acidified, however, it liberated iodine from a solution of potassium iodide, which would indicate that some hydrion was present in addition to an oxidising radicle. It is probable that the acidic substance was hypobromous acid.

When a solution of potassium bromide was added, a precipitate of silver bromide was obtained. This proved that the solution contained silver, but no bromide. The amount of silver bromide so obtained from 100 c.c. of solution was 0·10 gram, which is a little less than would be obtained from a saturated solution of silver bromate at the ordinary temperature.

The solution slowly deposited silver bromide, a decomposition which was accelerated by boiling. From 100 c.c. of a solution, which had been kept for a fortnight and then heated for some time on the steam-bath, 0·03 gram was deposited. This slow production of silver bromide was probably due to slow decomposition of the hypobromous acid into bromic and hydrobromic acids, with subsequent interaction between the silver bromate and hydrobromic acid.

There is therefore no evidence of the existence of silver hypobromite, even in solution. Bromine water appears to react with silver oxide just as it does with mercuric oxide. In both cases the bromide ions formed by the hydrolysis

$$Br_2 + H_2O = H^{\cdot} + Br' + HBrO$$

are removed from the solution by formation of insoluble or non-ionised bromide, and the reaction therefore continues with formation of hypobromous acid.

Silver Cyanate and Iodine.—The silver cyanate was prepared from silver nitrate and carbamide as described by Walker and Hambly (Trans., 1895, **67**, 746). It had been carefully dried and proved by analysis to be pure, although it darkened slightly on long exposure to light. Silver cyanate and iodine in presence of water reacted very slowly in the cold, but more quickly on boiling. The mixture evolved carbon dioxide steadily, and the characteristic odour of cyanic acid was noticeable. The reaction proceeded much faster when the solution was warmed, but the black colour of the iodine did not entirely disappear until the mixture had been heated for several hours on the steam-bath. From analogy to the reactions already described, the action which may be expected is that shown by the equation:

$$6AgCNO + 6I + 3H_2O = 5AgI + AgIO_3 + 6HCNO.$$

The insoluble residue was found to be silver iodide and iodate in agreement with this equation. The solution was at first strongly acid, but became neutral. On evaporation, a white, crystalline solid was obtained, which was found by qualitative analysis to be mainly carbamide, with traces of an organic silver salt and an iodine compound. Several recrystallisations from alcohol were necessary before the carbamide was obtained in a pure form. During the first evaporation to dryness a volatile substance with an extremely unpleasant odour was given off. The crystals obtained by the first crystallisation from alcohol blackened quickly in the light, although too little silver was present to yield even an opalescence with potassium iodide. The impurity after it had blackened was insoluble in alcohol, and could therefore be separated, but it was only entirely removed after four crystallisations from alcohol, although the amount present was extremely small. After four crystallisations from alcohol, the melting point was 131—132°, identical with that of a sample of pure carbamide in the same apparatus. It was identified by the biuret and other well-known reactions for carbamide. The nitrogen was estimated by Kjeldahl's method. (Found, N=46·6. Calc., N=46·7 per cent.)

The acid reaction and the odour of cyanic acid indicate that the first stage of this reaction is that indicated by the equation given above. Cyanic acid is unstable, and yields carbamide on boiling with water, so that the complete reaction may be represented by the equation already given, followed by the conversion of the cyanic acid into carbamide:

$$2HCNO + H_2O = CO(NH_2)_2 + CO_2.$$

In an experiment in which 30 grams of silver cyanate and 25 grams of iodine were boiled with water, the weight of carbamide after one crystallisation from alcohol was 4·1 grams. The yield of carbamide to correspond with the above equations would be 5·9 grams, so that there is no doubt that these equations represent the main reaction. There was some loss of cyanic acid as vapour, as was evidenced by the odour. No other substances were obtained in sufficient amount to be identified.

Note on the Decomposition of Cyanic Acid by Water.

The above representation of the reaction between silver cyanate, iodine, and water afforded a simple and satisfactory explanation of the experimental phenomena, but it appeared at first sight to be irreconcilable with certain statements in the literature as to the decomposition of cyanic acid by water. The main facts in regard to this action are briefly as follows:

(1) Cyanic acid, when liberated from a concentrated solution of potassium cyanate by cautious addition of acetic acid, yields, as the main product, potassium hydrogen cyanurate. The reaction is therefore similar to the polymerisation of anhydrous cyanic acid, and may be represented by the equation:

$$3HCNO = (HCNO)_3.$$

We would suggest that this is the typical mode of decomposition of non-ionised cyanic acid, and that formation of cyanuric acid will occur whenever non-ionised cyanic acid is present.

(2) It has been found (Cumming, Trans., 1903, **83**, 1391) that lead cyanate is decomposed by water with formation of lead carbonate and carbamide, the complete reaction being expressed by the equation:

$$Pb(CNO)_2 + 2H_2O = PbCO_2 + CO(NH_2)_2.$$

O. and I. Masson (*Zeitsch. physikal. Chem.*, 1910, **70**, 290) have found that the reaction is a general one for all metallic cyanates, and that the reaction takes place in two stages:

$$(1)\ CNO' + 2H_2O \longrightarrow NH_4CO_3' \rightleftharpoons NH_4^{\cdot} + CO_3''$$
$$(2)\ CNO' + NH_4^{\cdot} \longrightarrow CO(NH_2)_2.$$

The primary unimolecular reaction between the cyanate ions and water was found to be much slower than the secondary bimolecular reaction between the cyanate and ammonium ions (Walker and Hambly, *loc. cit.*). The experimental results of O. and I. Masson agree well with this hypothesis as to the course of the reaction with various metallic cyanates. The decomposition of cyanic acid differs, however, from that of a salt, such as barium cyanate, in that account must be taken of the effect of the hydrion concentration. With barium cyanate, the hydrion concentration probably becomes constant as soon as a precipitate of barium carbonate appears, and the hydrion therefore functions simply as a catalyst.

(3) Cyanic acid, when liberated from a cyanate by addition of a mineral acid, is decomposed with formation of an ammonium salt and carbon dioxide. With excess of a mineral acid, the whole of the cyanate is decomposed in this manner (Cumming and Masson, *Proc. Soc. Chem. Ind. Victoria*, 1903, 26 and 56). The complete reaction may be represented by the equation:

$$2H^{\cdot} + CNO' + H_2O = NH_4^{\cdot} + CO_2.$$

(4) With a pure cyanic acid solution, we should expect that each of the above reactions will play some part. In the first place, it may be pointed out that the neutral reaction of the alkali cyanates indicates that cyanic acid is a strong acid, and that it will therefore be highly ionised in dilute solution.

In dilute solution therefore the reaction

$$2H^{\cdot} + 2CNO' + H_2O = NH_4^{\cdot} + CNO' + CO_2$$

should occur. Since the hydrion disappears at twice the rate of the cyanate ion, this reaction will be complete when half the cyanate has been decomposed. The remaining cyanate ions should react with the ammonium ions with production of carbamide.

Liebig and Wöhler (*Ann. Phys. Chem.*, 1830, [ii], **20**, 369) found that cyanic acid reacted with water to yield ammonium hydrogen carbonate, whilst at the same time some carbamide and cyamelide were formed. Our experiments with silver cyanate and iodine had suggested that the main product of the decomposition of cyanic acid by water was carbamide, and some further experiments were therefore performed.

A solution of cyanic acid was prepared by mixing a measured volume of *N*-hydrochloric acid with slightly more than an equivalent amount of silver cyanate. The solution, after about an hour, became alkaline in reaction, and, on warming, evolved a little ammonia. Carbon dioxide was also given off, but there was no vigorous effervescence as described by Liebig and Wöhler, a difference due perhaps to the use of a less concentrated solution. After filtration, the precipitate was examined; it appeared to be silver chloride and cyanate only, with no cyanuric acid. The filtrate was evaporated to dryness, and yielded crude carbamide (melting at about 118°). In two experiments the yield of crude carbamide was determined.

Hydrochloric acid, c.c. of *N*-solution.	Weight of AgCNO added, grams.	Crude carbamide obtained, grams.	Calculated possible yield, grams.
100	16	2·8	3·0
280	45	7·0	8·4

During the evaporation to dryness there was a steady loss of carbon dioxide and ammonia, and a few milligrams of a white, insoluble residue separated before the carbamide began to crystallise. The insoluble residue, from qualitative tests, appeared to be cyanuric acid, and its separation was doubtless due to hydrolysis of ammonium cyanurate with loss of the ammonia during the evaporation. The residue was dissolved in alcohol, and filtered from the small amount of insoluble cyanuric acid. The filtrate, on evaporation to dryness, was found to be pure carbamide.

In *N*-solution therefore the main product of the decomposition of cyanic acid is carbamide, with a smaller amount of ammonium hydrogen carbonate and a trace of ammonium cyanurate.

The three modes of decomposition of aqueous cyanic acid may be expressed by the equations:

I. $3HCNO = (HCNO)_3$.

II. $CNO' + H_2O + 2H^{\cdot} = 2NH_4^{\cdot} + CO_2$.

III. $2H^{\cdot} + 2CNO' + H_2O = CO(NH_2)_2 + CO_2$.

The first equation gives the method of decomposition of non-ionised cyanic acid, and indicates the main reaction in concentrated solution. The second equation shows the action of acid on any cyanate, whilst the third equation indicates the main reaction in dilute solution when no other acid is present.

Silver Cyanate and Bromine.—When bromine water was added to silver cyanate there was a very vigorous reaction. In one experiment, when some liquid bromine was poured in with the bromine water, most of the mixture was driven out of the flask by the gas liberated. The gas was found to be a mixture of carbon dioxide and nitrogen. The insoluble residue was silver bromide, and contained no cyanuric acid. The filtrate, which was acid in reaction, was found to contain ammonium bromide, and, in somewhat smaller amounts, carbamide and ammonium cyanurate. Some hypobromous acid was also present.

The formation of nitrogen is probably due to secondary interaction between carbamide and hypobromous acid. With 50 grams of silver cyanate and a slight excess of bromine water (concentration not determined, but the solution was saturated at room temperature), about 100 c.c. of nitrogen was obtained. In this experiment the filtrate, on evaporation to dryness, yielded 9·8 grams of a deliquescent mixture, of which the main constituents were ammonium bromide, carbamide, and cyanuric acid.

The reaction appears therefore to resemble the reaction between silver cyanate and iodine, but is faster on account of the greater solubility and larger hydrolysis of the bromine. The secondary reactions are also much more marked, in agreement with the greater oxidising power of hypobromous as compared with iodic acid.

Silver Thiocyanate and Iodine.—When silver thiocyanate and iodine were shaken with water, there was an immediate production of silver iodide. If this action were analogous to that with silver acetate, then the products to be expected would be silver iodide, silver iodate, and thiocyanic acid, provided the silver thiocyanate were taken in excess.

Silver iodate, however, was not formed. The solution was found to contain sulphuric acid, hydrocyanic acid, ammonia, and carbon dioxide in addition to thiocyanic acid.

Some quantitative estimations of this reaction were made, in each case the silver thiocyanate being taken in excess of the amount calculated for the interaction of a molecule of silver thiocyanate and an atom of iodine.

In one experiment 3·967 grams of silver thiocyanate and 2·819 grams of iodine were mixed with water, and the whole was boiled and filtered. The precipitate, after being washed and dried, weighed 5·466 grams. Calculating on the supposition that all the iodine went to form silver iodide, one expected 5·218 grams of silver iodide and 0·269 gram of silver thiocyanate, a total weight of 5·487 grams. This agreement was satisfactory, since some iodine escaped as vapour on boiling the mixture.

In the following experiments the filtrate was made up to a known volume. The thiocyanic acid was estimated volumetrically by titration with standard silver nitrate, and the cyanide determined in another portion by Volhard's method, excess of sodium hydroxide and a drop of potassium iodide solution being first added. The presence of iodide ions is here necessary. Otherwise the soluble complex salt, $KAg(CNS)_2$, is also formed, and the true end-point of the formation of $KAg(CN)_2$ is not obtained. The ammonia was determined by boiling with excess of sodium hydroxide and titration of the distillate. The sulphuric acid was determined gravimetrically by precipitation with barium chloride.

Expt. I was carried out in the cold, the mixture being well shaken.

Expt. II. The mixture was boiled (when hydrogen cyanide must have escaped).

Expt. III. The mixture was boiled, and the distillate was received in standard sodium hydroxide. Nearly all the hydrogen cyanide distilled over, in addition to carbon dioxide.

The results are as follows, the numbers being given in gram-molecules, except in the case of iodine, which is given in gram-equivalents:

	I.		II.		III.	
Reacting substances.	Found.	Calc.	Found.	Calc.	Found.	Calc.
AgCNS ...	0·0398	—	0·0294	—	0·0313	—
I	0·0391	0·0322	0·0273	0·0262	0·0293	0·0289
Reaction products.						
HCNS......	0·0276	0·0276	0·0225	0·0225	0·0248	0·0248
HCN	0·0025	0·0023	[0·0007]	0·0019	0·0024	0·0021
H_2SO_4......	0·0047	0·0046	0·0037	0·0037	0·0042	0·0041
NH_3	(not estimated)	0·0023	0·0029	0·0019	0·0025	0·0021

The calculated values given in the table were obtained from the equation:

$$14AgCNS + 7I_2 + 10H_2O = 14AgI + 12HCNS + 2H_2SO_4 + HCN + NH_3 + CO_2,$$

the basis of calculation being the amount of thiocyanic acid produced. The calculations were not made from the amount of iodine originally weighed out, because some iodine escaped as vapour when the solutions were heated, and, when cold, the particules of iodine seemed to become coated with silver iodide.

Accordingly, the table shows the calculated values for iodine to be less than the experimental. Otherwise the agreement of the experimental with the calculated values is satisfactory. Unlike the reactions described above, this reaction results in the oxidation of part of the thiocyanic acid. The formation of the products actually obtained necessitates the supposition that two oxidations are proceeding simultaneously, namely:

$$HCNS + H_2O + 3O = HCN + H_2SO_4,$$

$$\text{and } HCNS + 2H_2O + 4O = H_2SO_4 + NH_3 + CO_2.$$

The equation for the whole reaction corresponding with these oxidations are respectively:

$$6AgCNS + 3I_2 + 4H_2O = 6AgI + 5HCNS + HCN + H_2SO_4,$$

and

$$8AgCNS + 4I_2 + 6H_2O = 8AgI + 7HCNS + H_2SO_4 + NH_3 + CO_2.$$

It follows that the actual reaction must have proceeded equally in each of these directions, since by the addition of these two equations there is obtained the equation with which the experimental results agree, namely:

$$14AgCNS + 7I_2 + 10H_2O = 14AgI + 14HCNS + 2H_2SO_4 + HCN + NH_3 + CO_2.$$

Silver Sulphite and Iodine.—From the experiments with silver thiocyanate and iodine it appeared probable that, whenever the primary reaction led to the formation of an oxidisable acid, an oxidation product would be obtained. In accord with expectations, it was found that silver sulphite and iodine yielded only silver iodide and sulphuric acid, even when the silver sulphite was taken in excess:

$$Ag_2SO_3 + I_2 + H_2O = 2AgI + H_2SO_4.$$

Silver Thiocyanate and Chlorine.—Silver chloride is more soluble than the thiocyanate, the solubilities at 20° being: AgCNS, $8 \cdot 27 \times 10^{-7}$ gram-molecules per litre, and AgCl, $1 \cdot 06 \times 10^{-5}$ gram-molecules per litre. In the introduction it was suggested as a working hypothesis that the interaction of a silver salt and a halogen depends on the hydrolysis of the halogen in aqueous solution. Any silver salt with an ionic concentration above 3×10^{-9} should, if this hypothesis is correct, react with a saturated chlorine solution. In spite of its lower solubility therefore, silver thiocyanate should yield silver chloride on treatment with a saturated chlorine solution.

It was found that interaction occurred at the ordinary temperature, but that the action did not proceed to completion. (The action should stop when the chlorine concentration has fallen to a certain value even if some silver thiocyanate be present. This point was only tested qualitatively.) The products of the reaction were: silver chloride; sulphuric, hydrocyanic, and hydrochloric acids; and ammonia.

Potassium Cyanate and Bromine.—As the potassium cyanate used in these experiments contained some carbonate, it was analysed, the carbonate being precipitated as barium carbonate, and the cyanate as silver cyanate. These analyses gave the factor for actual potassium cyanate present as 0·929, and for carbon dioxide as 0·0420. Bromine water acted immediately at the ordinary temperature on a solution of potassium cyanate. A gas containing carbon dioxide and nitrogen was evolved, and an examination of the liquid after the excess of bromine was boiled off proved the presence of potassium and ammonium bromide.

In a series of quantitative experiments excess of bromine was added to a solution containing a known amount of potassium cyanate. The solution was then boiled under a reflux condenser until it became colourless. The gas evolved was led through a series of tubes containing (1) sulphuric acid, (2) phosphoric oxide, (3) red phosphorus, which had been dried in a vacuum desiccator and which retained the excess of bromine, (4) and (5) soda-lime.

The carbon dioxide produced was determined from the weights of the soda-lime tubes before and after the experiments.

The solution was made up to a known volume, and from portions of this, both bromide and ammonium were volumetrically determined.

The results, given in gram-equivalents, were as follows:

	Substance, gram.	CO_2.		Br.		NH_3.	
		Found.	Calc.	Found.	Calc.	Found.	Calc.
1.	0·6905	[0·00952]	0·00827	0·01290	0·01260	0·00279	0·00395
2.	0·6234	0·00770	0·00747	0·01185	0·01138	0·0025	0·00357
3.	0·6674	0·00785	0·00800	0·01170	0·01218	0·00273	0·00383

In experiment (1) the red phosphorus had not been properly dried, so that hydrogen bromide passed over into the soda-lime tubes, and probably caused the carbon dioxide result to be too high. In order to estimate the nitrogen liberated, a solution containing a known amount of potassium cyanate was placed in a flask closed by a rubber cork, through which there was fitted a long glass tube which served as a condenser and was closed at the top by a glass tap. The flask and tube were exhausted by means of a Töpler air-pump. Excess of bromine was allowed to enter the flask by means of the tube, and the solution was then boiled, the stop-cock being closed. The flask was again exhausted, the gas evolved being led through a tube of soda-lime and fused calcium chloride to remove the water vapour, carbon dioxide, and bromine. The nitrogen was collected in a measuring tube over mercury, and was measured at atmospheric pressure.

The ammonium salt in solution in the flask was also estimated.

The experimental results are given below in gram-equivalents.

In experiment *A* there were taken 50 c.c. of a solution containing 0·7568 gram of the impure potassium cyanate dissolved in 250 c.c. of water. In each of the experiments *B* there were taken 25 c.c. of a solution containing 3·045 grams dissolved in 500 c.c. of water:

		KCNO corrected.	Nitrogen obtained as gas.	NH_3 in solution.	Total N obtained.
A	...	0·00868	0·00488	0·00397	0·00885
B.	1.	0·0349	0·0193	0·0165	0·0358
	2.	0·0349	0·0207	0·0135	0·0342
	3.	0·0349	0·0186	0·0168	0·0354

The calculated values given in the tables have been obtained from the equation:

$$4KCNO + 4H_2O + 3Br_2 = 4KBr + 2NH_4Br + N_2 + 4CO_2.$$

The results show that the main reaction is according to this equation. The amounts of ammonia, however, are consistently lower, and those of nitrogen higher, than their calculated values, although the total nitrogen is well accounted for. Possibly this is due to a side reaction, namely, the action of a hypobromite on carbamide. The carbamide could be formed from ammonium and cyanate ions, which must be in solution together during the progress of the reaction, and hypobromite would be formed by the action of bromine on the carbonate originally present with the cyanate.

Silver Acetylide and Iodine.—The action of iodine on silver acetylide in presence of water was found to be quite unlike the reactions described above. Reaction occurred very slowly, and it was found that for each atom of silver present at least two atoms of iodine were required. The insoluble residue appeared to be a mixture of silver iodide and acetylide. The filtrate was extracted with ether, and on evaporating the ether a very small residue, the vapour of which attacked the eyes and possessed an extremely unpleasant odour, was obtained.

It is probable that this residue contained the substance $C_4H_2I_4$, crystals of which Berend (*Annalen*, 1865, **135**, 258) obtained by the action of an ethereal solution of iodine on silver acetylide.

Silver Acetate and Cyanogen Iodide.—This reaction was examined in the hope that silver iodide would be formed, together with some product of the interaction of the cyanogen and acetate radicles, but this did not take place.

The cyanogen iodide was prepared by subliming the precipitate obtained by the addition of iodine to a solution of potassium cyanide.

Quantities in the ratio of a molecule of cyanogen iodide to a molecule of silver acetate were weighed out and dissolved in water. A white precipitate was slowly formed, but even after four days this precipitation was not complete. The precipitation was slightly accelerated by boiling the solution, but on continuing the evaporation to dryness a considerable amount of silver acetate was found to be still undecomposed. During this evaporation the cyanogen iodide must have been lost, for when the solution was boiled under a reflux condenser, solid cyanogen iodide was found to condense within the condenser. The precipitate obtained in this reaction was a mixture of silver cyanide, iodide, and iodate.

The action of cyanogen iodide therefore on silver acetate appears to be similar to that of iodine, but the slowness of the reaction is probably due to the excessively small number of ions it forms in water. It may be noted that when a solution of potassium hydroxide was added to the original solution, a copious precipitate of silver iodide immediately appeared.

Summary.

The halogens react with silver salts to yield an insoluble silver halide, an acid, and one or more oxidation products of either the acid or the halide. A simple, typical case is the action of iodine on silver acetate, which is represented by the equation:

$$3I_2 + 3H_2O + 5C_2H_3O_2Ag = 5AgI + HIO_3 + 5C_2H_4O_2.$$

The reactions, on account of secondary oxidations, are sometimes complex; for example, silver thiocyanate and iodine interact according to the equation:

$$14AgCNS + 7I_2 + 10H_2O = 14AgI + 12HCNS + 2H_2SO_4 + HCN + NH_3 + CO_2.$$

The oxidation reactions were much more marked with chlorine and bromine than with iodine, on account probably of the greater oxidising power of hypochlorous and hypobromous acids as compared with iodic or hypoiodous acids.

The main product obtained by treatment of silver cyanate by iodine was carbamide, formed probably by secondary decomposition of cyanic acid. Bromine and silver cyanate yield ammonium bromide, carbamide, cyanuric acid, and a little nitrogen.

For comparison the interaction of bromine and potassium cyanate was studied, and found to be in accord with the equation:

$$4KCNO + 4H_2O + 3Br_2 = 4KBr + 2NH_4Br + N_2 + 4CO_2.$$

It is suggested that the reactions are due to interactions with the products of the hydrolysis of the halogen by water; thus, a silver salt reacts with the halide ions formed by partial hydrolysis of the halogen, for example:

$$Cl_2 + H_2O = H^{\cdot} + Cl' + HClO.$$

Further interaction may occur between the hypochlorous acid and one of the other reaction products.

The experimental results are in accord with this hypothesis.

In connexion with the formation of carbamide, some experiments on the decomposition of aqueous cyanic acid were tried, and these, in conjunction with previous work, led to the conclusion that cyanic acid decomposes in three different ways according to the conditions of experiment. In concentrated solution the main reaction is the formation of cyanuric acid, probably by polymerisation of non-ionised cyanic acid molecules. Acids decompose cyanic acid according to the equation:

$$CNO' + H_2O + 2H^{\cdot} = 2NH_4^{\cdot} + CO_2.$$

In dilute solution cyanic acid decomposes itself, according to the above equation, until all the hydrion has been used up. The ammonium ions and the remaining cyanate ions interact to form carbamide. The whole reaction is expressed by the equation:

$$2H^{\cdot} + 2CNO' + H_2O = CO(NH_2)_2 + CO_2.$$

In conclusion we desire to take this opportunity of expressing our indebtedness to Prof. James Walker for his valuable advice and criticism throughout the research.

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CXCVII.—*The Refraction and Dispersion of Triazo-compounds. Part II.*

By James Charles Philip.

The data recorded in the previous investigation (Trans., 1908, **93**, 918) led to the adoption of 8·91 as the mean refraction value and 0·36 as the mean dispersion value ($H_\gamma - H_\alpha$) of the N_3-group. These figures were based on the investigation of ethyl triazoacetate, ethyl α-triazopropionate, ethyl β-triazopropionate, ethyl bistriazoacetate, triazoethyl alcohol, bistriazoethane, and benzylazoimide. The refraction and dispersion values for the N_3-group were obtained by subtracting from the experimental figures for molecular refraction and dispersion the sum of the contributions of the other atoms in the molecule. If in this operation the newer figures for atomic refraction and dispersion adopted by Eisenlohr (*Zeitsch. physikal. Chem.*, 1910, **75**, 585; see also Roth and Eisenlohr, "Refractometrisches Hilfsbuch") are employed, the mean refraction and dispersion values for the N_3-group, deduced from the data for the above-mentioned compounds, become 8·95 and 0·35 respectively.

The refractive power and density of various other triazo-compounds, prepared in Dr. Forster's laboratory, have now been determined, and the data obtained lead to 8·90 and 0·348 as the mean refraction and dispersion values for the N_3-group. On reviewing the whole of the experimental material available for deducing the most probable refraction and dispersion values, it was considered advisable to omit the results for ethyl bistriazoacetate. Owing, perhaps, to the fact that the two triazo-groups in this substance are attached to the same carbon atom, both refraction and dispersion values are distinctly outside the general range. When ethyl bistriazoacetate is left out of account, the mean refraction and dispersion values to be adopted for the N_3-group in ordinary positions become 8·91 and 0·348 respectively.

As shown in the previous communication, there are certain triazo-compounds in which the refraction and dispersion values of the N_3-group are distinctly enhanced. The cases where such an "optical exaltation" was recorded were ethyl triazoformate, phenylazoimide, and α-naphthylazoimide. These are all compounds in which the triazo-group is attached to a doubly-linked carbon atom, and it was suggested that the enhancement of optical values observed here is comparable with the exaltation found in compounds which contain contiguous unsaturated groups. Further support for this view is furnished by the results of the present investigation. Of the new triazo-compounds examined, there are two—*o*-triazoiodobenzene and αγ-bistriazopropylene—in which the N_3-group is attached to a doubly-linked carbon atom, and in both these cases the refraction and dispersion values are notably enhanced.

The similarity of the triazo group and the bromine atom in relation to the values of the optical constants, alluded to in the earlier communication, has been further emphasised by a comparative study of certain triazo-compounds and the corresponding bromine compounds. It should be noted that Eisenlohr's new figures for the atomic refraction and dispersion of bromine are 8·865 and 0·340 respectively.

EXPERIMENTAL.

The determinations of density and refractive index were carried out at 25·0° ± 0·1° (corr.). As far as possible, the compounds were examined immediately after they had been distilled. Details of the preparation of the triazo-compounds investigated have already been published in three papers by Forster and his collaborators

(Trans., 1911, **99**, 1277; this vol., 489, 1359). The experimental data for the triazo-compounds and certain others which were examined for comparative purposes are recorded in table I.

TABLE I.

Substance.	d_4^{25}.	n_α.	n_D.	n_β.	n_γ.
β-Triazoethylamine	1·0429	—	1·4635	—	—
γ-Triazopropylamine	1·0043	—	1·4615	—	—
αβ-Bistriazopropyl alcohol	1·2860	1·5032	1·5068	—	1·5226
αγ-Bistriazo*iso*propyl alcohol	1·2631	1·4999	1·5033	—	1·5189
α-Triazo-γ-chloro*iso*propyl ,,	1·3011	1·4903	1·4933	—	1·5071
αβ-Bistriazo-γ-chloropropane ...	1·3203	1·5038	1·5073	—	1·5233
αγ-Bistriazo-β-chloropropane ...	1·2999	1·5000	1·5035	—	1·5191
o-Triazoiodobenzene	1·8893	—	1·6631	—	—
αγ-Bistriazopropylene	1·1572	1·5148	1·5202	1·5342	—
o-Bromoiodobenzene..............	2·2571	—	1·6618	—	—
o-Dichlorobenzene	1·2934	1·5424	1·5476	1·5602	1·5712
o-Chlorobromobenzene...........	1·6382	1·5729	1·5786	1·6113	—
o-Chloroiodobenzene	1·9515	1·6262	1·6331	1·6691	—
αβ-Dibromopropyl alcohol	2·1259	1·5538	1·5577	—	1·5757
αγ-Dibromo*iso*propyl alcohol ...	2·1202	1·5458	1·5495	—	1·5661
αγ-Dibromopropylene	1·9952	1·5339	1·5378	1·5495	—

From the densities and refractive indices of the first seven triazo-compounds in the foregoing table, the values of the molecular refraction $[MR]_D = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{d}$ and of the molecular dispersion $[MR]_\gamma - [MR]_\alpha$ have been calculated. On subtracting from these experimental figures the sum of the refraction and dispersion values for the other atoms in the molecules, the contributions of the N_3-group to the refraction and dispersion respectively are obtained as shown in table II. Eisenlohr's values for atomic refraction and dispersion have been used in these calculations, namely: refraction for *D*-line: C, 2·418; H, 1·100; O (hydroxyl), 1·525; Cl, 5·967; N (primary aliphatic amine), 2·322: dispersion, $H_\gamma - H_\alpha$: C, 0·056; H, 0·029; O (hydroxyl), 0·015; Cl, 0·168.

TABLE II.

			Contribution of N_3-group to	
Substance.	$[MR]_D$.	$[MR]_\gamma - [MR]_\alpha$.	Refraction.	Dispersion.
β-Triazoethylamine	22·76	—	9·00	—
γ-Triazopropylamine	27·38	—	9·00	—
αβ-Bistriazopropyl alcohol	32·87	1·057	8·75	0·350
αγ-Bistriazo*iso*propyl ,,	33·28	1·056	8·95	0·350
α-Triazo-γ-chloro*iso*propyl alcohol	30·28	0·876	8·93	0·351
αβ-Bistriazo-γ-chloropropane	36·22	1·168	8·75	0·344
αγ-Bistriazo-β-chloropropane	36·55	1·168	8·91	0·344

One of the substances in the foregoing table, γ-triazopropylamine, has been examined also by Curtius (*Ber.*, 1912, **45**, 1090), who deduces 8·82 and 0·33 for the refraction and dispersion values of the N_3-group. The same author (*ibid.*, 1047) has deduced the values 8·85 and 0·30 from measurements of the refraction and dispersion of ethyl γ-triazobutyrate. These figures are somewhat lower than the mean of those obtained in this and the previous investigation.

Of the triazo-compounds enumerated in table I there remain for consideration *o*-triazoiodobenzene and αγ-bistriazopropylene, substances in which the N_3-group is attached to a doubly-linked carbon atom. The value of $[MR]_D$ for *o*-triazoiodobenzene, based on the figures in table I, is 48·05. If the refraction value for the rest of the molecule is subtracted, 10·04, a notably enhanced figure, is obtained for the refraction equivalent of the N_3-group. The enhancement is clearly indicated also by a comparison of the figure 48·05, the molecular refraction of *o*-triazoiodobenzene, with 46·37, the corresponding figure for *o*-bromoiodobenzene. The normal refraction value for the N_3-group is only about 0·05 unit higher than that for the bromine atom, and hence in the ordinary course the molecular refractions of *o*-triazoiodobenzene and *o*-bromoiodobenzene would be nearly equal. This is plainly not the case.

In this connexion the question may be raised whether the molecular refraction of the halogen derivatives of benzene is not abnormal. According to Seubert (*Ber.*, 1889, **22**, 2519), the observed values for the molecular refraction of these compounds are invariably lower than the calculated values, the difference amounting in some cases to 0·5 unit. It was thought worth while, in connexion with the comparison instituted between *o*-triazoiodobenzene and *o*-bromoiodobenzene, to see whether there are similar differences between the observed and calculated values of the molecular refraction in the case of the ortho-dihalogen derivatives of benzene. With this object in view, specimens of *o*-dichlorobenzene, *o*-chlorobromobenzene, and *o*-chloroiodobenzene, prepared by Mr. Barnett, were subjected to refractometric investigation. The experimental values obtained for the molecular refraction of these compounds, based on the constants recorded in table I, are compared in table III with the corresponding values calculated (*a*) from the old figures for atomic refraction, (*b*) from Eisenlohr's new figures. For the sake of comparison, Seubert's values for the molecular refraction of the monohalogen derivatives are incorporated in the table.

TABLE III.

		$[MR]_D$ calculated.	
	$[MR]_D$ found.	*a.*	*b.*
Chlorobenzene	31·05	31·38	31·17
Bromobenzene	33·88	34·31	34·07
Iodobenzene	38·99	39·50	39·11
o-Chlorotoluene	35·69	35·98	35·79
o-Bromotoluene	38·50	38·91	38·69
o-Dichlorobenzene...........	36·06	36·33	36·04
o-Chlorobromobenzene	38·81	39·26	38·94
o-Chloroiodobenzene.........	43·64	44·45	43·97
o-Bromoiodobenzene	46·37	47·38	46·87

In the case of the dihalogen derivatives, also, there is seen to be a very marked discrepancy between the observed values of the molecular refraction and those calculated from the old figures for atomic refraction. The table, however, brings out the interesting result that these discrepancies largely disappear, both for the monohalogen and for the dihalogen compounds, when the calculated values are based on Eisenlohr's new figures for atomic refraction. The discrepancies, it is true, do not disappear altogether, but the table demonstrates clearly the superiority of the new atomic refraction values over the old ones. In the case of *o*-bromoiodobenzene, the observed molecular refraction is still 0·5 lower than the calculated value, and in comparing the molecular refractions of *o*-triazoiodobenzene and *o*-bromoiodobenzene, it is necessary to bear this in mind. Even, however, if the calculated value for *o*-bromoiodobenzene be taken as the basis of comparison, the existence of an exaltation in the refraction value of the triazo-compound is sufficiently clear.

In $\alpha\gamma$-bistriazopropylene we have another case in which the triazo-group is attached to a doubly-linked carbon atom, and in which, as might be expected, there is distinct optical exaltation. The experimental value of the molecular refraction of this compound, based on the constants in table I, is 32·61, and the dispersion $[MR]_\beta - [MR]_\alpha$ is 1·019. If the refraction equivalent for three C-atoms, four H-atoms, and one double bond is subtracted from 32·61, the remainder is 19·22, attributable to the two N_3-groups. This figure itself is considerably more than double the normal refraction value for the N_3-group, but it is probable that the exaltation is due solely to that N_3-group which is attached to the doubly-linked carbon atom. It is practically certain that the other N_3-group, being attached to a fully saturated carbon atom, makes the normal contribution to the molecular refraction.

The very notable optical exaltation exhibited by $\alpha\gamma$-bistriazopropylene is very well brought out by a comparison of the refraction and dispersion values for the bistriazo- and dibromo-derivatives of propyl alcohol, *iso*propyl alcohol, and propylene. The values of $[MR]_D$ for $\alpha\beta$-dibromopropyl alcohol, $\alpha\beta$-bistriazopropyl alcohol, $\alpha\gamma$-dibromo*iso*propyl alcohol, and $\alpha\gamma$-bistriazo*iso*propyl alcohol are 33·03, 32·87, 32·72, and 33·28 respectively, while the corresponding values for $[MR]_{\gamma}-[MR]_{\alpha}$ are 1·063, 1·057, 0·995, 1·056. As might be expected from the practical equality in the refractive and dispersive power of the bromine atom and the triazo-group, the figures for the four compounds do not differ markedly from one another.

It is instructive to contrast with this agreement the figures for $\alpha\gamma$-dibromopropylene and $\alpha\gamma$-bistriazopropylene. The values of $[MR]_D$ for these compounds are 31·33 and 32·61 respectively, while the values for $[MR]_{\beta}-[MR]_{\alpha}$ are 0·755 and 1·019. These figures show clearly that in the case of $\alpha\gamma$-bistriazopropylene, as in that of *o*-triazoiodobenzene, the attachment of the N_3-group to a doubly-linked carbon atom involves a notable enhancement of the optical values.

I have much pleasure in acknowledging my indebtedness to Dr. Forster, Dr. Withers, and Mr. Barnett, who furnished me with the material for this investigation.

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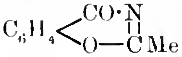
CXCVIII.—*The Action of Acyl Chlorides on Primary Amides.*

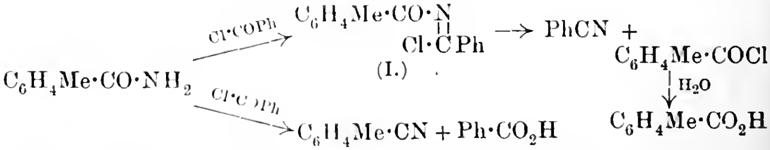
By ARTHUR WALSH TITHERLEY and THOMAS HALSTEAD HOLDEN.

ALTHOUGH the action of acyl chlorides on amides in the presence of pyridine has been closely studied by one of the authors, and by others, very little appears to be known concerning the interaction which takes place when an acyl chloride and amide are heated together. Preliminary observations which were made in the course of this investigation made it clear that the reaction was by no means simple, and that a variety of products might result the nature of which depended on the conditions of the reaction. Experiments were accordingly instituted with the object of throwing light on the mechanism of the reaction occurring between an acyl chloride and amide by selecting acetyl and benzoyl chlorides, on the one hand, and acetamide, benzamide, and *p*-toluamide on the other.

In a previous communication it has been shown by one of the authors (Trans., 1911, **99**, 867) that salicylamide and acetyl chloride readily react, yielding the hydrochloride of the cyclic compound  $C_6H_4\left<\begin{matrix}CO\cdot N\\ O{-}CMe\end{matrix}\right.$. As this hydrochloride was, from its behaviour with aniline, at first believed to be the chloro-compound $OH\cdot C_6H_4\cdot CO\cdot N\colon CMeCl$, it appeared likely that the first stage in the reaction between a primary amide and acyl chloride might be a process of condensation leading to a chloro-compound of the type $\cdot CO\cdot N\colon CRCl$, the water eliminated then decomposing a second molecule of acyl chloride in the usual way, thus:

$$\cdot CO\cdot NH_2 \xrightarrow{2R\cdot COCl} \cdot CO\cdot N\cdot CRCl + R\cdot CO_2H + HCl.$$

Although very close search was made for such chloro-derivatives by treatment with aniline, in no case was any indication of their presence obtained, but large quantities of acid and nitrile always appeared. Since, however, chloro-compounds of the above type would be thermo-labile, as has been proved in the case of the compound $PhCO\cdot N\colon CPhCl$, examined by Titherley and Worrall (Trans., 1910, **97**, 839), which rapidly decomposes at 100° into benzonitrile and benzoyl chloride, it would therefore be difficult to isolate such compounds formed in the course of a reaction which, as a rule, only takes place on heating. When benzoyl chloride and benzamide, for example, are heated to 140°, large quantities of benzonitrile and benzoic acid are formed, together with a small quantity of dibenzamide. At lower temperatures the action, which is much slower, yields a higher, although still small, proportion of dibenzamide. It is clear that the production of benzonitrile and benzoic acid would be consistent with the intermediate production of the chloro-compound $PhCO\cdot N\colon CPhCl$, but it is equally explicable otherwise (see below). The action of benzoyl chloride on *p*-toluamide was studied with a view to settling the question as to whether an intermediate chloro-compound of the above type preceded nitrile formation, for, if formed, such a hypothetical chloro-compound (I) should yield benzonitrile; whilst if nitrile formation were due to dehydration of the amide, *p*-toluonitrile should result, thus:



As a result of a number of experiments which have been tried, it has been shown that, besides benzo-*p*-toluamide, both *p*-toluonitrile and benzonitrile (together with benzoic acid and *p*-toluic acid) may be formed. As, however, in the mixed nitriles, *p*-toluonitrile always predominates, and as it is practically the sole product when an excess of *p*-toluamide is employed, it would appear that the production of benzonitrile is not due to the above hypothetical mechanism, but is connected with some secondary decomposition, probably that of the benzo-*p*-toluamide, which, under the catalytic influence of hydrogen chloride, could decompose in two possible ways, thus:

$$\begin{tikzcd}[row sep=small] & C_6H_4Me\cdot CN + Ph\cdot CO_2H \\ C_6H_4Me\cdot CO\cdot NH\cdot COPh \arrow[ur] \arrow[dr] & \\ & PhCN + C_6H_4Me\cdot CO_2H \end{tikzcd}.$$

A similar decomposition has been observed with dibenzamide, which at 140°, under the catalytic influence of hydrogen chloride, yields benzonitrile and benzoic acid; and in further support of this view it has been found that in the reaction between *p*-toluamide and benzoyl chloride, under varying conditions, the yields of secondary amide and benzonitrile are inversely related, that is, benzonitrile is formed at the expense of a diminished yield of benzo-*p*-toluamide. Thus, at 140°, when three molecular proportions of *p*-toluamide to one of benzoyl chloride are taken, a considerably higher yield of benzo-*p*-toluamide (with practically no benzonitrile) is found than when equimolecular proportions are taken (a considerable quantity of benzonitrile being formed). This difference is to be attributed to the fixation of the hydrogen chloride by the amide when an excess of the latter is used, yielding *p*-toluamide hydrochloride, $C_6H_4Me\cdot CO\cdot NH_2,HCl$, which was isolated in quantity.

In general, the facts established make it clear that in the action of benzoyl chloride on an aromatic amide two distinct reactions occur, one (to a relatively small extent) leading to direct benzoylation, and the other to what is virtually dehydration, thus:

$$\begin{tikzcd}[row sep=small] & Ar\cdot CO\cdot NH\cdot COPh \quad A. \\ Ar\cdot CO\cdot NH_2 \arrow[ur, "Ph\cdot COCl"] \arrow[dr, "Ph\cdot COCl"'] & \\ & Ar\cdot CN + Ph\cdot CO_2H \quad B. \end{tikzcd}$$

That reaction *B* is independent of *A*, and that the production of nitrile and acid does not mainly arise by secondary decomposition of the secondary amide first formed, appears to follow from the fact that even when an excess of amide is taken and the hydrogen chloride (which alone is effective in causing decomposition of the secondary amide) is largely fixed, the actual amount of secondary amide is still small.

No appreciable reaction occurs below 100°, and the influence of increasing temperature is greatly to increase the apparent velocity of reaction *B* and depress the yield of secondary amide, the reaction being complete at 140° in six hours. This easy dehydration of aromatic amides is probably not a direct reaction, but one in which an unstable benzoyl derivative of the imino-ester type (III) is first formed by benzoylation of the pseudomeric form of the amide (II), benzoic acid being subsequently eliminated:

$$\underset{\text{(II.)}}{\mathrm{Ar{\cdot}C(OH){:}NH}} \xrightarrow{\mathrm{Ph{\cdot}COCl}} \underset{\text{(III.)}}{\mathrm{Ar{\cdot}C(O{\cdot}COPh){:}NH}} \longrightarrow \mathrm{Ar{\cdot}CN + Ph{\cdot}CO_2H}$$

On the other hand, the production of secondary amide may be attributed to direct benzoylation of the normal amide form ($\cdot\mathrm{CO{\cdot}NH_2}$) by loss of hydrogen chloride from the intermediate hypothetical additive compound (IV).

$$\underset{\text{(IV.)}}{\mathrm{Ar{\cdot}CO{\cdot}NH_2,Ph{\cdot}COCl}} \xrightarrow{-\mathrm{HCl}} \mathrm{Ar{\cdot}CO{\cdot}NH{\cdot}COPh}.$$

If this view is correct, the low yields of secondary amide must be attributed to a higher chemical activity of the pseudomeric form in the equilibrium mixture:

$$\mathrm{Ar{\cdot}CO{\cdot}NH_2} \rightleftharpoons \mathrm{Ar{\cdot}C(OH){:}NH},$$

but it is impossible at present to say how far the reduced yield of secondary amide at higher temperature is due to higher concentration of the pseudomeric amide or to the catalytic decomposition of the former by hydrogen chloride. Experiments will be instituted to throw light on the nature of the decomposition by hydrogen chloride of mixed secondary amides.

Owing to the above simultaneously occurring changes in the action between *p*-toluamide and benzoyl chloride, the following products appear in varying proportions according to the conditions: *p*-toluamide hydrochloride, *p*-toluonitrile, benzoic acid, and benzo-*p*-toluamide, together with benzonitrile and *p*-toluic acid. The amount of the last compound was usually more than would be expected to arise by the decomposition of benzo-*p*-toluamide, and, further, ammonium chloride was also found. These two substances appear to arise from a secondary decomposition between *p*-toluamide hydrochloride and hydrogen chloride, and, in order to elucidate this point, the action of hydrogen chloride on benzamide and *p*-toluamide was investigated. Both these amides readily yield hydrochlorides as white, crystalline solids, which dissociate incompletely at 140°, and are somewhat soluble in benzoyl chloride. When heated at 140° for several hours in an atmosphere of hydrogen chloride, they are largely decomposed, giving ammonium chloride and the corresponding acyl chloride, which then reacts as above with a portion of the dissociated free amide, so that varying mixtures may result containing ammonium chloride, acyl chloride, acid nitrile, and secondary amide, according to the duration of heating. This decomposition is probably preceded by the formation of an additive compound (V) of amide and hydrogen chloride, involving opening up of the carbonyl group, thus:

$$\mathrm{Ar{\cdot}CO{\cdot}NH_2,HCl} \longrightarrow \underset{\text{(V.)}}{\mathrm{Ar{\cdot}CCl(OH){\cdot}NH_2}} \xrightarrow{\mathrm{HCl}} \mathrm{Ar{\cdot}COCl + NH_4Cl}.$$

This action at once explains why *p*-toluic acid and ammonium chloride appear in the reaction between benzoyl chloride and *p*-toluamide. Di-*p*-toluamide, which should also be produced, was not detected, probably on account of its small quantity.

The action of benzoyl chloride on acetamide, which has already been the subject of study by Pinner (*Ber.*, 1892, **25**, 1435) and one of the authors (Trans., 1901, **79**, 412), follows on a similar mechanism (*B*) to that of benzoyl chloride on aromatic amides, without production of secondary amide, but it takes place with very much greater velocity, and is nearly complete at 80° in five minutes, yielding acetonitrile (which polymerises slightly) and benzoic acid, together with acetamide hydrochloride in large quantity. It is thus evident that the velocity of reaction *B*, involving condensation with the pseudomeric form of acetamide, is enormously higher than the corresponding reaction with aromatic amides. Small quantities of benzoic anhydride are also found as a by-product, and its origin has been traced to a secondary action between benzoyl chloride and benzoic acid under the influence of acetamide as a remover of hydrogen chloride. Benzoic anhydride has been shown by the authors to be formed in moderate quantity, even in absence of acetamide, by the action of benzoyl chloride on benzoic acid at 80°, by the reversible change:

$$\mathrm{BzCl + BzOH \rightleftharpoons Bz_2O + HCl}.$$

but the yield, as might be expected, is greatly increased by the presence of acetamide. This observation is in accordance with the fact established by Brooke (*J. Amer. Chem. Soc.*, 1912, **34**, 492), that acetyl chloride and acetic acid, by a reversible reaction, yield small quantities of acetic anhydride; whilst conversely the authors have observed that acetic anhydride is rapidly decomposed in the cold by hydrogen chloride, yielding acetyl chloride and acetic acid.

The action of acetyl chloride on simple amides differs from that of benzoyl chloride in that it takes place more readily and leads mostly to acetylation, thus:

$$\mathrm{{\cdot}CO{\cdot}NH_2 + CH_3{\cdot}COCl \longrightarrow {\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_3 + HCl}.$$

This has already been shown to be the case by one of the authors with acetamide (Titherley, Trans., 1901, **79**, 411). It has now been shown that a considerable yield of acetobenzamide is produced by the continued action of acetyl chloride, at its boiling point, on benzamide. No evidence of any intermediate chloro-compound could be obtained by examination of the product after treatment with aniline, but traces of benzanilide were found showing the presence of benzoyl chloride. The production of benzoyl chloride evidently arises as a secondary decomposition between benzamide hydrochloride and hydrogen chloride, as already discussed.

EXPERIMENTAL.

Benzoyl Chloride and Benzamide.

The two substances were heated together in a reflux apparatus, moisture being excluded by means of a phosphoric oxide tube. The following observations were made:

1. At 80°: no appreciable reaction in twelve hours.

2. At 95°: 12 grams of benzamide (1 mol.) and 14 grams of benzoyl chloride (1 mol.) were heated at this temperature for eight hours.

Slow action occurred, and hydrogen chloride was slowly evolved. The latter, which was absorbed by passing into water, amounted to 1·88 grams. The reaction product in the flask contained, besides unchanged benzoyl chloride and benzamide, benzamide hydrochloride, small quantities of benzoic acid and benzonitrile, and 5 grams of dibenzamide, which, after crystallisation from aqueous alcohol, melted at 148°. (Found, N = 6·56. Calc., N = 6·30 per cent.)

3. At 125°: 12 grams of benzamide (1 mol.) and 52 grams (3 mols.) of benzoyl chloride were heated at this temperature for six hours, when the reaction was nearly complete. Two grams of hydrogen chloride were evolved, and from the liquid reaction product 3·7 grams of dibenzamide, which mostly crystallised out, were obtained. Large quantities of benzoic acid and benzonitrile were also obtained.

4. At 145°: 12 grams of benzamide (1 mol.) and 21 grams of benzoyl chloride (1·5 mols.) were heated at this temperature for twenty hours. 3·45 Grams of hydrogen chloride were evolved. The reaction product contained 1·5 grams of dibenzamide, 11·5 grams of benzoic acid, and 9 grams of benzonitrile.

Benzoyl Chloride and p-*Toluamide.*

Similar observations were made to those with benzamide on the influence of temperature on the course of the reaction, and attention was chiefly directed to the nature and amount of the products obtained at 140°, after complete reaction, and disappearance of the benzoyl chloride.

The treatment was as follows. The reaction product, which became semi-solid on cooling, was treated with benzene, and the insoluble *p*-toluamide hydrochloride, $C_6H_4Me\cdot CO\cdot NH_2,HCl$, together with a little ammonium chloride, collected and washed. The benzene filtrate was shaken with 10 per cent. aqueous sodium hydroxide in order to remove the acids (benzoic and *p*-toluic) and benzo-*p*-toluamide, and the alkaline extract was acidified with hydrochloric acid without delay so as to avoid decomposition of the secondary amide. The precipitate, after washing, was digested with aqueous sodium hydrogen carbonate, and the insoluble benzo-*p*-toluamide collected. It was practically pure, and melted before recrystallising at 114°. (Found, N = 5·64. Calc., N = 5·8 per cent.) Its properties were identical with those described by Wheeler, Johnson, and McFarland (*J. Amer. Chem. Soc.*, 1903, **25**, 787). The mixed acids, present in the filtrate after treatment with sodium hydrogen carbonate, were recovered by acidification, and the proportion of benzoic to *p*-toluic acid in the mixture was ascertained in two experiments by analysis of the mixed silver salts. The above benzene solution, after being washed with alkali, was immediately dried by sodium sulphate and saturated with dry ammonia to remove any acyl chloride as amide, but, with the proportions of reacting substances used (shown in the table), it was found that there was no appreciable quantity of acyl chloride present. The benzene was removed by distillation, and the residue treated with light petroleum in order to separate *p*-toluamide, which remained insoluble. After distilling off the light petroleum from the filtrate, the residual oil was fractionated. The liquid distillate consisted of a mixture of *p*-toluonitrile (mainly) and benzonitrile, and its composition was arrived at in one case by an estimation of nitrogen. In one experiment, when three molecular proportions of *p*-toluamide to one of benzoyl chloride were employed, the distillate consisted of almost pure *p*-toluonitrile, and immediately solidified on cooling. The following table shows the yields obtained, corrected for any loss due to solubility, and expressed on the same weight (10 grams) of benzoyl chloride.

Ratio of mols. of *p*-toluamide to mols. of benzoyl chloride.	*p*-Toluamide.	Temp.	Time.	Benzoic acid.	*p*-Toluic acid.	Benzo-*p*-toluamide.	*p*-Toluamide hydrochloride and ammonium chloride.	*p*-Toluonitrile.	Benzonitrile.
1 : 1	9·7	120°	8 hrs.	7·1	1·3	0·84	trace	5·0	
1 : 1	10·0	130	12 ,,	2·25		4·0	—	1·0	
1 : 1	9·7	140	6 ,,	8·4		0·56	0·56	3·5	0·7
0·85 : 1	8·3	140	14 ,,	4·2		1·1	—	2·7	
1 : 1	10·0	140	14 ,,	4·3		2·4	—	—	
3 : 1	26·1	140	6 ,,	6·1	4·8	2·4	4·35	8·5	trace

Action of Hydrogen Chloride on p-*Toluamide and Benzamide.*

A slow stream of dry hydrogen chloride was passed into 4 grams of *p*-toluamide at 140—150°, moisture being excluded. *p*-Toluoyl chloride and *p*-toluonitrile were slowly formed, and appeared as a liquid in the neck of the flask. After heating seven hours, the reaction product was examined by treating with benzene, when 2·3 grams of *p*-toluamide hydrochloride and 0·5 gram of ammonium chloride remained. The benzene filtrate, after treating as described on p. 1877, yielded *p*-toluic acid (0·2 gram), *p*-toluoyl chloride (0·25 gram), *p*-toluonitrile (0·3 gram), and di-*p*-toluamide (0·04 gram)—the latter melting at 155—156°, and being identical in properties with the compound described by Krafft and Karstens (*Ber.*, 1892, **25**, 454).

From these figures, which are low owing to mechanical loss, it is clear that the *p*-toluamide has been converted primarily into *p*-toluoyl chloride, which, by subsequent action on *p*-toluamide, has yielded the corresponding secondary amide, nitrile, and acid, these overlapping reactions occurring under the above conditions to the extent of about 30 per cent. of complete decomposition.

The ammonium chloride formed by elimination of ammonia was found itself to be without influence on the course of the reaction, although it was at first suspected catalytically to bring about decomposition of an amide into nitrile and acid. By heating 4 grams of *p*-toluamide with 1 gram of ammonium chloride at 160—170° for six hours, it was shown that no decomposition of the amide had taken place.

Similar observations to the action of hydrogen chloride on *p*-toluamide have been made in the case of benzamide, which slowly decomposes at 140° in presence of gaseous hydrogen chloride, yielding, besides benzamide hydrochloride and ammonium chloride, benzoyl chloride, benzoic acid, benzonitrile, and small quantities of dibenzamide, the yields being similar to those obtained in the case of *p*-toluamide.

Action of Hydrogen Chloride on Dibenzamide.

Three grams of dibenzamide were heated for four and a-half hours at 145° to 150° in an atmosphere of hydrogen chloride. The solid (m. p. 148°) gradually liquefied as decomposition occurred. No benzoyl chloride was formed, but benzoic acid and benzonitrile were produced in quantity. From the mixture 1·6 grams of benzoic acid were isolated (calc. for complete decomposition 1·63 grams). Owing to the difficulty of preventing loss of benzonitrile its yield was not determined.

At 140° the decomposition was considerably slower, and proceeded to the extent of only 24 per cent. in four hours.

Benzoyl Chloride and Acetamide.

Benzoyl chloride and acetamide react slowly even in the cold, and very rapidly at 80°, the temperature at which the reaction was studied. As acetamide hydrochloride, $(CH_3{\cdot}CO{\cdot}NH_2)_2,HCl$, is always formed, three molecular proportions of acetamide were usually taken for each molecular proportion of benzoyl chloride. At 80° a homogeneous liquid is formed, from which acetamide hydrochloride is rapidly deposited, the reaction being apparently complete in five minutes, and a yellow, semi-solid mass resulting. On treatment with benzene, the filtrate from the acetamide hydrochloride was shaken with 10 per cent. aqueous sodium hydroxide in order to isolate the acid (benzoic). The residual benzene solution, after removing the benzene, gave an oil, which, after heating on the water-bath to remove any unchanged benzoyl chloride and being subsequently treated with aqueous sodium carbonate, left benzoic anhydride, which crystallised on keeping. No ammonium chloride was formed. Acetonitrile, which is always produced, was identified in a separate experiment by direct distillation, after ten minutes' heating. The liquid, which did not pass over until the temperature was raised considerably, boiled at 80°, and possessed the usual properties of acetonitrile. The yield was slightly less than that required by theory owing to slight polymerisation.

The following table shows the proportions yielded when the time and ratios of benzoyl chloride to acetamide were varied (expressed on 4·21 grams of benzoyl chloride = 1 mol.).

Temperature 80°.

Acetamide.	Benzoyl chloride.	Time in minutes.	Acetamide hydrochloride, grams.	Benzoic acid, grams.	Benzoic anhydride, grams.	Acetonitrile, grams.
3 mols.	1 mol.	15	3·5	1·87	0·5	—
3 ,,	1 ,,	60	—	1·7	0·95	—
2 ,,	1 ,,	15	3·0	1·35	0·79	—
3 ,,	1 ,,	10	—	—	—	1·0

These figures indicate that an increased yield of benzoic anhydride is obtained by longer heating or by relative increase in the amount of benzoyl chloride, and it thus appeared to arise secondarily from the action of the benzoyl chloride on the benzoic acid formed. This was confirmed by (i) heating benzoyl chloride and benzoic acid together at 80° for one hour, and (ii) heating a mixture of acetamide and benzoic acid with benzoyl chloride. In (i) molecular proportions were taken, and 4·21 grams of benzoyl chloride were found to yield 0·59 gram of benzoic anhydride. In (ii) two molecular proportions of acetamide, one of benzoic acid, and one of benzoyl chloride (4·21 grams) yielded 3·0 grams of benzoic anhydride. This high yield of benzoic anhydride, in comparison to the yields obtained above, shows that acetamide disturbs the equilibrium between benzoyl chloride and benzoic acid, yielding the anhydride by removing the hydrogen chloride. In order to make sure that the benzoic anhydride did not arise, as it conceivably might by decomposition, through water, of an imino-ester, $CH_3 \cdot C(OBz){:}NH$, experiments were instituted involving treatment of the reaction product without intervention of water.

4·21 Grams of benzoyl chloride and 5·31 grams of acetamide were heated for fifteen minutes at 80°, and the benzene filtrate from the acetamide hydrochloride was treated with light petroleum, which separated a yellow oil. The oil, on washing with light petroleum (b. p. 35—45°), partly solidified, yielding crystals of impure acetamide (m. p. 68—75°), which remained on treatment with pure ether; benzoic acid, together with a little benzoic anhydride (total 0·2 gram) being removed. The light petroleum solution and washings contained also only benzoic acid, with some benzoic anhydride (total 2·5 grams), besides a little benzoyl chloride. No evidence could be obtained of an imino-benzoate. Further, in another experiment the reaction product, after removing acetamide hydrochloride, and subsequently the benzene, was fractionated. Benzoic acid passed over in quantity between 228° and 280°, leaving a small amount of benzoic anhydride in the distilling flask.

Acetyl Chloride and Benzamide.

Acetyl chloride and benzamide react slowly at the boiling point of the mixture, yielding acetobenzamide in large quantity. A considerable excess over the theoretical quantity of acetyl chloride was used. Twenty grams of benzamide and 105 grams of acetyl chloride were heated to boiling in a reflux apparatus for sixteen hours, care being taken to exclude moisture. After distilling off the excess of acetyl chloride from a water-bath, a red oil remained, which deposited acetobenzamide as a yellow solid on cooling. The crude product weighed 23 grams (theory requires 27 grams), and after crystallising from dilute alcohol the pure compound was obtained in colourless needles, melting at 116—117°.

Small quantities of benzoic acid and benzoyl chloride were also produced in the reaction, but no appreciable quantity of benzonitrile. In one experiment, after heating 12 grams of benzamide and 40 grams of acetyl chloride for sixteen hours and subsequently distilling off the excess of acetyl chloride, the product was treated with 9 grams of aniline dissolved in pure ether, in order to ascertain whether any chloro-compound was present. Practically no reaction occurred, and the solid, which separated after washing with water, consisted of acetobenzamide (6·5 grams). The ethereal solution, on removing the ether, left a mixture of aniline and a further quantity of acetobenzamide, together with a small quantity of acetanilide and benzanilide. By shaking with a large volume of water and digesting the resulting solid with aqueous sodium hydroxide to remove acetobenzamide, acetanilide and benzanilide remained, which were separated by boiling with light petroleum. The insoluble benzanilide (0·2 gram), after crystallisation from aqueous acetone, melted at 160°, and a mixture of the substance with pure benzanilide melted at 160—161°. The appearance of benzanilide after treatment with aniline shows that a small quantity of benzoyl chloride is formed in the action of acetyl chloride on benzamide, but benzoylphenylacetamidine, $CH_3\cdot C(NHPh){:}N\cdot COPh$, which was specially looked for was not present.

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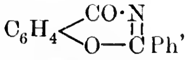
CXCIX.—*The Action of Benzotrichloride on Primary Amides.*

By ARTHUR WALSH TITHERLEY and THOMAS HALSTEAD HOLDEN.

THE investigation of the action of benzotrichloride on simple amides arose out of an observation made in the condensation of benzotrichloride and salicylamide, where, instead of the expected 2-phenyl-1 : 3-benzoxazine-4-one,



$C_6H_4{<}\begin{matrix}CO\cdot N\\ O{-}\overset{\|}{C}Ph\end{matrix}$

a large yield of *o*-benzoyloxybenzonitrile, $BzO\cdot C_6H_4\cdot CN$, resulted. In order to throw light on the mechanism of this change the action of benzotrichloride on benzamide was first studied. It was found that, although it takes place less readily than in the case of salicylamide (which reacts at 80°), at 140° fairly rapid action occurs, yielding benzoyl chloride and benzonitrile in large quantity, together with benzoic acid and a small quantity of dibenzamide, the change being fairly complete in an hour. As it appeared that this change was one of condensation followed by decomposition, two alternative processes, *A* and *B*, might underlie it, involving the normal and pseudomeric form of the amide, thus:

$$A.\quad \mathrm{Ph\cdot CO\cdot NH_2 \xrightarrow{PhCCl_3} Ph\cdot CO\cdot NH\cdot CCl_2Ph \xrightarrow{-HCl} Ph\cdot CO\cdot N{:}CPhCl \xrightarrow{split} Ph\cdot COCl + Ph\cdot CN}$$

$$B.\quad \mathrm{Ph\cdot C(OH){:}NH \xrightarrow{PhCCl_3} Ph\cdot C(OCCl_2Ph){:}NH \xrightarrow[split]{-HCl} Ph\cdot CN + Ph\cdot COCl.}$$

In mechanism *A* the presumed intermediate compound, $\mathrm{Ph\cdot CO\cdot N{:}CPhCl}$, which, as shown by Titherley and Worrall (Trans., 1910, **97**, 839), is thermo-labile and decomposes into benzoyl chloride and benzonitrile, could not survive a temperature of 140° without decomposition. An alternative hypothesis, in which benzotrichloride functions as a dehydrating agent, thus yielding benzonitrile, is not consistent with the ease of the reaction or with the production of benzoyl chloride instead of benzoic acid, since separate experiments established the fact that benzoic acid and benzotrichloride only yield small quantities of benzoyl chloride under the conditions of the reaction (20 per cent. of the total possible in six hours at 140°). From the experiments which have been carried out, as described below, under various conditions, there can be no doubt that in the action of benzotrichloride on an amide the first recognisable products of the change are benzoyl chloride and a nitrile, and that the other products which are found arise secondarily.

In order to decide between mechanism *A* and *B*, the case of benzotrichloride and *p*-toluamide was studied, since in this case the identity of nitrile and acyl chloride resulting must differ according to the course of the preliminary condensation. Thus, while with *A* a mixture of *p*-toluoyl chloride and benzonitrile would result, with *B* benzoyl chloride and *p*-toluonitrile would be obtained:

$$A.\quad \mathrm{C_6H_4Me\cdot CO\cdot NH_2 \xrightarrow{PhCCl_3} C_6H_4Me\cdot CO\cdot NH\cdot CCl_2Ph \xrightarrow{-HCl} C_6H_4Me\cdot CO\cdot N{:}CPhCl \xrightarrow{split} C_6H_4Me\cdot COCl + Ph\cdot CN}$$

$$B.\quad \mathrm{C_6H_4Me\cdot C(OH){:}NH \xrightarrow{PhCCl_3} C_6H_4Me\cdot C(OCCl_2Ph){:}NH \xrightarrow[split]{-HCl} C_6H_4Me\cdot CN + Ph\cdot COCl.}$$

It was found that (in addition to the secondary products, benzoic and *p*-toluic acids, benzo-*p*-toluamide, *p*-toluamide hydrochloride, and ammonium chloride) both *p*-toluoyl chloride and benzonitrile, on the one hand, and benzoyl chloride and *p*-toluonitrile on the other, were produced in relative proportions which greatly varied with the conditions of the reaction. In nearly all cases benzoyl chloride and *p*-toluonitrile predominated, and, in fact, only very small quantities of *p*-toluoyl chloride and benzonitrile were formed when the proportions of *p*-toluamide to benzotrichloride taken were 3 mols.: 1 mol., at 140°. On the other hand, when equimolecular proportions were taken (at 140° for six hours) 25 to 50 per cent. of the resulting acyl chloride and nitrile consisted of *p*-toluoyl chloride and benzonitrile. These variations appeared to be less dependent on temperature than on relative concentration and time. At 130° practically the same observations were made as at 140°, but when equimolecular proportions of *p*-toluamide and benzotrichloride were heated for only one hour at 140° (the reaction being incomplete), the main product was benzoyl chloride and *p*-toluonitrile.

An explanation of these remarkable variations was sought along various lines. The possibility of interaction, analogous to double decomposition, between *p*-toluonitrile and benzoyl chloride or benzoic acid or benzotrichloride, which might yield benzonitrile, was considered, but excluded by separate experiments with these substances, carried out under the same conditions as that of the reaction between benzotrichloride and *p*-toluamide; in no case was any action observed. It was finally proved that relatively large quantities of benzonitrile (40 per cent. of the mixed nitriles) were produced when *p*-toluamide hydrochloride was heated with benzotrichloride for one hour at 140°, the reaction being incomplete. This fact at once renders intelligible the variations described above, and it would appear that *p*-toluamide reacts largely in its normal form (mechanism *A*) when liberated continuously by dissociation of its hydrochloride, whilst it reacts mainly in its pseudo-form (mechanism *B*) when present in the free condition. The following changes therefore are involved in the reaction between benzotrichloride and *p*-toluamide. Initially the course of the reaction follows mechanism *B* almost exclusively (and in this respect it is similar to that observed by the authors in the action of benzoyl chloride: this vol., p. 1873). A small proportion of the total number of amide molecules may react as in *A* (compare the action of benzoyl chloride on *p*-toluamide at 140°, *loc. cit.*). As the reaction proceeds, owing to the formation of hydrogen chloride, *p*-toluamide hydrochloride (which is soluble in the reaction mixture) is formed, and reacts under concomitant dissociation with benzotrichloride, this reaction largely following the course *A*, thus yielding *p*-toluoyl chloride and benzonitrile,* the amount of which therefore increases with time.

When an excess of *p*-toluamide (3 mols.: 1 mol.) is initially taken, it appears not only to facilitate the reaction by removing the hydrogen chloride formed, but as an equivalent amount is also present to the end of the reaction as free *p*-toluamide, the reaction follows course *B* almost exclusively.

In addition to the above primary reactions, certain secondary changes occur between a portion of the *p*-toluamide and the acyl chlorides on the one hand, and hydrogen chloride on the other. These reactions, which have been studied independently and already described (*loc. cit.*), lead to the production of benzoic and *p*-toluic acids, benzo-*p*-toluamide, and di-*p*-toluamide, together with *p*-toluonitrile (by the action of the acyl chlorides on *p*-toluamide), and to the production of *p*-toluonitrile, *p*-toluoyl chloride, and *p*-toluic acid, together with ammonium chloride (by the action of hydrogen chloride on *p*-toluamide). In practice all these by-products were found in proportions which necessarily varied with the conditions of the reaction. Traces of benzoic anhydride were also found. In general, large quantities of benzoic and *p*-toluic acids, and correspondingly small amounts of the acyl chlorides (practically none on long heating), were produced when three molecular proportions of *p*-toluamide and one of benzotrichloride were taken. On the other hand, when equimolecular proportions of the two latter were taken, a large yield of acyl chlorides resulted, and a correspondingly small yield of acids. The yield of secondary amides (chiefly benzo-*p*-toluamide) was always small, and was highest when the proportions of *p*-toluamide to benzotrichloride were 3 mols.: 1 mol. These facts are consistent with the theory considered above as to the mechanism of the reaction. Throughout there is a complete parallel between the action of benzotrichloride and that of benzoyl chloride on any aromatic amide.

The similarity also extends to acetamide, which reacts fairly readily at 80° with benzotrichloride, yielding, besides acetamide hydrochloride, acetonitrile and benzoic acid. No benzoyl chloride is found although evidently it is at first formed, and this must be attributed to its very rapid action on acetamide, yielding benzoic

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* It is probable that benzonitrile also arises partly by the decomposition of some of the benzo-*p*-toluamide formed secondarily by the action of the benzoyl chloride produced on *p*-toluamide. It has been shown by the authors (*loc. cit.*) that secondary amides readily suffer fission under the catalytic influence of hydrogen chloride into an acid and nitrile, and thus benzo-*p*-toluamide would yield a mixture of benzoic and *p*-toluic acids together with benzonitrile and *p*-toluonitrile.

acid (compare *loc. cit.*). It is evident that acetamide reacts exclusively in its pseudomeric form with benzotrichloride, as it does with benzoyl chloride.

EXPERIMENTAL.

Salicylamide and Benzotrichloride.

Forty grams of salicylamide and 60 grams of benzotrichloride were heated at 110—120° for three hours, during which steady action took place with evolution of hydrogen chloride. On cooling, the liquid set to a nearly solid mass, which was washed with light petroleum. The solid (55 grams) consisted of a mixture of *o*-benzoyloxybenzonitrile (mainly) and *N*-benzoylsalicylamide, which were separated by digestion with an excess of cold dilute ammonia. The alkaline filtrate, on acidification, yielded 4 grams of *N*-benzoylsalicylamide, melting, after recrystallisation from alcohol, at 205°. The insoluble solid consisted of practically pure *o*-benzoyloxybenzonitrile, and weighed 48 grams (75 per cent. of theory). After recrystallisation from alcohol, it separated in colourless needles, melting at 106—107°, identical in all its properties with a specimen of *o*-benzoyloxybenzonitrile obtained by benzoylation of salicylonitrile.

The conditions of the condensation were varied in several experiments, but the best yield of *o*-benzoyloxybenzonitrile was obtained as above. The reaction takes place readily in presence of boiling acetic acid, and even in boiling benzene (that is, at about 80°). No appreciable reaction, however, takes place in boiling ether.

Benzamide and Benzotrichloride.

No action takes place in boiling benzene solution, in six hours (compare salicylamide). Five grams of benzamide (1 mol.) and 8 grams of benzotrichloride (1 mol.) were heated at 140° in a reflux apparatus, when a fairly vigorous reaction set in, hydrogen chloride being rapidly evolved during the first thirty minutes. After heating six hours, the hydrogen chloride, which was estimated by absorption in water and titration, amounted to 3 grams (theory, for 2 mols. HCl, requires 3·1 grams.) The reaction product, on cooling, formed a yellow liquid, having a strong odour of benzoyl chloride. No free benzamide was present. After treatment with light petroleum and filtering from traces of benzamide hydrochloride and ammonium chloride, the liquid was shaken with aqueous sodium hydroxide to remove benzoic acid (0·9 gram) and dibenzamide (0·2 gram), which were recovered by acidification and separated by digestion with aqueous sodium hydrogen carbonate.

The dried light petroleum solution containing benzoyl chloride was, without delay, saturated with dry ammonia, and yielded 2·28 grams of benzamide, equivalent to 2·64 grams of benzoyl chloride. The filtrate from the benzamide and ammonium chloride, on distilling, yielded 4·2 grams of benzonitrile and 1·7 grams of unchanged benzotrichloride, which was removed (see p. 1887) by treatment with sulphuric acid.

p-*Toluamide and Benzotrichloride.*

In the action between *p*-toluamide and benzotrichloride, which was carried out similarly to that between benzamide and benzotrichloride, the effect of varying conditions was closely followed. At 140° vigorous evolution of hydrogen chloride continued for about thirty minutes, and then gradually subsided. The yellowish-brown product, which, after cooling, varied from a semi-solid mass, when an excess of amide was employed, to a mobile liquid, when equimolecular proportions had been heated for six hours, was treated as below with the object of ascertaining the yield of the various substances formed. The reaction product was treated with benzene, and the insoluble *p*-toluamide hydrochloride and ammonium chloride, if present, were collected. The amount of ammonium chloride was small, and, in one case, at 130°, analysis of the washed solid showed that it consisted of nearly pure *p*-toluamide hydrochloride, $C_6H_4Me{\cdot}CO{\cdot}NH_2,HCl$. (Found, HCl = 20·97. Calc., HCl = 21·27 per cent.) The benzene filtrate was saturated with dry ammonia gas * in order to convert the acyl chlorides into amides, and acids into ammonium salts. The precipitate, after drying, was washed with water, the insoluble amides were collected, and the composition of the mixture when desired was arrived at by estimation of nitrogen. In one case separation of the amides (melting between 126° and 147°) was effected by repeated fractional crystallisation from hot water. *p*-Toluamide, melting at 160°, was easily obtained from the less soluble fractions, but benzamide, which appeared in the more soluble fractions, was never obtained perfectly pure, and finally melted at 119° (instead of 128°) after four recrystallisations. It was found to be extremely difficult to obtain pure benzamide from a mixture of benzamide and *p*-toluamide. From the weights of the respective amides (with a correction for the small amount dissolved in the benzene solution and isolated as described below) the yields of benzoyl chloride and *p*-toluoyl chloride in the original reaction product were calculated.

From the above aqueous extract (ammonium salts) the mixed acids (benzoic and *p*-toluic) were isolated by acidification, and the

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* Ammonia is without action on benzotrichloride in benzene solution.

composition of the mixture arrived at by analysis of the mixed silver salts,* correction in the yields being allowed for owing to loss due to the slight solubility. The benzene filtrate, after the above ammonia treatment, contained the mixed nitriles and secondary amides, together with small quantities of benzamide, *p*-toluamide, and benzotrichloride. It was shaken with cold 10 per cent. aqueous sodium hydroxide, and the secondary amides, thus extracted, were immediately precipitated by acidification. The mixture consisted of benzo-*p*-toluamide (chiefly) and di-*p*-toluamide, which were in one experiment separated by repeated fractional crystallisation from 80 per cent. alcohol, and finally absolute alcohol, by which means needles of di-*p*-toluamide were eventually obtained (melting at 148·5°); the benzo-*p*-toluamide appearing in the mother liquors and precipitated by water melted at 108°. The low melting points in each case show that perfect separation had not been effected, but the quantities were too small to achieve this or permit of analysis.

The mixed nitriles, present in the benzene solution after washing with alkali, were separated from any unchanged benzotrichloride and the small quantity of mixed amides by distilling off the benzene and treating the residual oil with light petroleum (b. p. 35—45°) to precipitate the mixed amides, the amounts of which were included in the correction referred to above. The light petroleum was removed from the filtrate and the residual oil then dissolved in cold 98 per cent. sulphuric acid, and treated with a little water in order to decompose the benzotrichloride.

After being kept for five to ten minutes at 40—50°, the mixture was treated with excess of water, the oil extracted with ether, and the benzoic acid removed by shaking the ethereal solution with alkali. (From the weight of recovered benzoic acid the amount of benzotrichloride was calculated, it having been previously shown that the conversion into benzoic acid by this treatment is quantitative.) In this treatment a very small quantity only of the nitriles pass into the corresponding amides. The mixed nitriles, after removing the ether, were weighed and fractionated. It was found that when the proportion of benzonitrile in the mixture did not exceed about 10 per cent., the *p*-toluonitrile in the distillate at once solidified (m. p. 29° after being kept on porous porcelain); otherwise the distillate remained more or less completely liquid. The presence of benzonitrile in the latter cases was established by complete hydrolysis and isolation of pure benzoic acid from the mixed acids by repeated fractional crystallisation from hot water. The composition of the mixed nitriles, except in those cases where

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* The titration method of ascertaining the composition of the mixture of acids, which was tried, gave untrustworthy values.

nearly pure *p*-toluonitrile only was obtained, was arrived at by estimation of nitrogen in the distillate. The above procedure was modified in some cases by reversing the order of treatment with ammonia and alkali described above.

The yields obtained are shown in the table below, and are expressed on the same weight (10·13 grams) of *p*-toluamide, when the time, temperature, and concentration of benzotrichloride were varied.

Ratio of mols. of *p*-toluamide : mols. of benzotrichloride.	Benzotrichloride.	Temp.	Time.	Unchanged benzotrichloride.	*p*-Toluamide hydrochloride.	Benzoyl chloride.	*p*-Toluoyl chloride.
1 : 1	14·65	130°	4 hrs.	3·2	4·0	4·4	
1 : 1	14·65	140	6 ,,	trace	nil	4·92	5·0
1 : 1	14·65	140	6 ,,	0·3	nil	8·6	
1 : 1	14·65	140	1 ,,	2·3	trace	4·0	1·0
3 : 1	4·88	100–130	10 ,,	nil	1·3	trace	trace
3 : 1	4·88	140	6 ,,	nil	2·7	trace	trace
3 : 1	4·88	140	3 ,,	nil	—	1·1	

Ratio of mols. of *p*-toluamide : mols. of benzotrichloride.	Benzoic acid.	*p*-Toluic acid.	Benzo-*p*-toluamide.	Benzonitrile.	*p*-Toluonitrile.
1 : 1	0·1	0·01	—	—	—
1 : 1	0·6	0·21	0·05	3·5	3·5
1 : 1	1·0	0·16	trace	2·1	6·3
1 : 1	2·1	0·22	0·15	1·0	5·7
3 : 1	1·1	2·25	1·0	0·35	4·45
3 : 1	1·0	1·5	0·33	0·49	4·4
3 : 1	1·55	2·0	1·5	trace	4·5

p-*Toluamide Hydrochloride and Benzotrichloride.*

Equivalent quantities were heated for one hour at 140°, and the product was examined by the previously described treatment in order to ascertain the composition of the resulting liquid nitrile mixture. 0·169 by Kjeldahl's method required 15·2 c.c. $N/10$-HCl. This corresponds with a mixture of 42 per cent. of benzonitrile and 58 per cent. of *p*-toluonitrile.

Acetamide and Benzotrichloride.

The reaction, which occurs with moderate speed at 80°, was carried out with varying proportions, but as acetamide hydrochloride, $(CH_3{\cdot}CO{\cdot}NH_2)_2,HCl$, is always produced, it was necessary to take a considerable excess of acetamide in order to complete the reaction. In one experiment 5·32 grams of acetamide (3 mols.) and 5·85 grams of benzotrichloride (1 mol.) were heated with repeated shaking at 80° for five hours, when no further reaction appeared to take place. On raising the temperature, acetonitrile distilled over, and was identified in the usual way. The semi-solid mass in the flask, after cooling, was treated with ether, and the insoluble acetamide hydrochloride (5·4 grams) collected. (Found, HCl = 23·5. Calc., HCl = 23·6 per cent.)

The ethereal solution contained 2·1 grams of benzoic acid and about 3 grams of unchanged benzotrichloride. No benzoyl chloride or benzoic anhydride were found. From the large amount of unchanged benzotrichloride, it was evident that a much higher proportion of acetamide is necessary for complete interaction. Taking 7·1 grams (8 mols.) of acetamide and 2·9 grams (1 mol.) of benzotrichloride, only 0·5 gram of the latter remained unchanged, and 6 grams of acetamide hydrochloride were obtained, together with 1·3 grams of benzoic acid, after heating for five hours at 80°.

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CC.—*Carbon Disulphide as Solvent for the Determination of the "Refraction Constant."*

By Frédéric Schwers.

In a former paper (*Mém. Acad. roy. Belg.*, 1911; *J. Chim. phys.*, 1910—1911) on the "refraction constant," I have shown the important results which the study of aqueous solutions of inorganic and organic substances can give regarding the changes in properties which occur on mixing two liquids. Water is very convenient for such a research, because of its total, or partial, miscibility with a great number of liquids, and also because the changes in density and refractive index are generally fairly large—a very favourable condition for their accurate determination.

There are, however, a great number of cases in which the investigations are prevented because of the complete insolubility in water of numerous organic liquids; and when only very dilute solutions can be prepared, the results are too uncertain. Amongst other suitable liquids possessing great solvent power, carbon disulphide—as I have already pointed out (*Bull. Acad. roy. Belg.*, 1912, 56)—is to be placed directly after water for several reasons:

(1) Besides its great solubility in numerous organic liquids, it is fairly easy to prepare in a pure state.

(2) Carbon disulphide is a useful material for the purpose of comparison with water in its solutions, because there is usually an expansion on mixing: aqueous solutions, on the contrary, are generally formed with contraction. Moreover, the changes are fairly large, and thus easy to measure accurately.

(3) The large dispersive power of carbon disulphide is naturally to be found partly in its solutions; the influence of the dispersion on the refraction constant is thus more easy to study than in the case of aqueous solutions.

Up to the present I had calculated the values of A only for those mixtures which have been examined by other investigators (*Bull. Acad. roy. Belg.*, 1912, 57); three binary systems which I myself examined presented anomalies, namely, carbon disulphide and chloroform, carbon disulphide and stannic chloride, and carbon disulphide and ethyl ether (*Bull. Acad. roy. Belg.*, 1912, 263).

In this paper I desire to show the variations of the refraction constant A in an organic series, and therefore examined three fatty acids (acetic, *iso*butyric, and *iso*valeric). The solubility of carbon disulphide in these acids increases with the increase of CH_2-groups in the molecule. The behaviour of water is exactly the opposite. In formic acid, the hydroxy-groups predominate, and the solubility in carbon disulphide is only slight. In the case of acetic acid the miscibility may be considered as infinite, although, at the laboratory temperature, separation occurs at certain concentrations, which makes the experiments somewhat difficult. Looking through the bibliography concerning the solubility curves of binary mixtures, I did not find any experiment regarding that point, although it appears to be of interest to investigate the matter.

The apparatus which I had the privilege of using was that employed by the late Sir William Perkin; and I am very much indebted to his son, Dr. F. Mollwo Perkin, who kindly allowed me to work in his laboratory. The refractometer with water-jacket and heating device has been minutely described (Trans., 1892, **61**, 287; 1896, **69**, 1035), so that there is no need to give any account of it here. The light employed by me was given by a Geissler-tube containing mercury vapour; the suitable rays are fairly similar to those of hydrogen, but have the advantage of giving greater intensity, so that they can be used also in the polarimetric determinations, allowing thus an easy comparison between those measures. The rays employed are: $\lambda = 496\mu\mu$ (blue) and $\lambda = 436\mu\mu$ (beginning of violet). In addition I employed the red line of hydrogen ($\lambda = 656{\cdot}3$) and the sodium *D*-line ($\lambda = 589{\cdot}3\mu\mu$) in preference to the yellow mercury light, which is a doublet ($\lambda = 579$ and $577\mu\mu$). The green ray ($\lambda = 546\mu\mu$), which I shall discuss in a future paper on magnetic rotation, was not used, as it is very close to the *D*-ray, and its determination was superfluous for my purpose.

For the density determinations, the pyknometer used consisted of a small flask carrying a thermometer through the stopper, and fitted with a side capillary tube, through which the excess of liquid could escape. The whole apparatus, containing about 47 c.c., is placed in a water-bath thermostat.

Acetic Acid + Carbon Disulphide.

The density of these mixtures undergoes a fairly large dilatation (up to 2·5 per cent.); a noticeable increase of expansion takes place at higher temperatures.

Densities determined:

Acetic acid.		Carbon disulphide.	
$t°$.	$d_{4°}^{t°}$.	$t°$.	$d_{4°}^{t°}$.
12·5°	1·05819	13·45°	1·27348
23·9	1·04546	22·6	1·25983
30·4	1·03797	33·95	1·24283

The densities and C_v-values of the solutions are given in the following table, in which d is the observed density; d_v the theoretical density, calculated from the formula $\frac{p_1 + p_2}{\frac{p_1}{d_1} + \frac{p_2}{d_2}}$, where p_1 and p_2 are the percentage weight of each constituent, d_1 and d_2 their respective densities; C_v the contraction of the density expressed in per cent. and calculated by means of the formula $\frac{d - d_v}{d}$.

I.—*Acetic Acid,* 12·076 *per cent.* + *Carbon Disulphide,* 87·924 *per cent.*

$t°$.	$d_{4}^{t°}$.	d_v.	$d_v : d$.	C_v.
13·5°	1·22831	1·24268	1·01171	−1·171
20·6	1·21786	1·23248	1·01200	1·200
30·8	1·20261	1·21767	1·01252	1·252

II.—*Acetic Acid,* 61·284 *per cent.* + *Carbon Disulphide,* 38·716 *per cent.*

14·7°	1·10562	1·13001	1·02206	−2·206
22·7	1·09475	1·12007	1·02313	2·313
30·7	1·08355	1·11011	1·02451	2·451

III.—*Acetic Acid*, 80·298 *per cent.* + *Carbon Disulphide*, 19·702 *per cent.*

$t°$.	$d^{t°}_4$.	d_v.	$d_v : d$.	C_v.
13·0°	1·07807	1·09426	1·01502	−1·502
20·7	1·06871	1·08520	1·01543	1·543
30·1	1·05643	1·07395	1·01658	1·658

The refractive index was also determined at three temperatures, and for the four above-mentioned rays, designated by r (red), D (yellow), b (blue), and v (violet).

Acetic Acid.

$t°$.	r.	D.	b.	v.
21·2°	1·36949	1·37146	1·37621	1·37952
31·7	1·36542	1·36738	1·37209	1·37536
49·7	1·35818	1·36014	1·36476	1·36798

Carbon Disulphide.

6·85°	1·62853	1·63816	1·66346	1·68620
20·9	1·61754	1·62694	1·65180	1·67436
34·5	1·60678	1·61588	1·64017	1·66225

For the solutions the figures are as follows: (n is the observed refractive index; n_v the theoretical refractive index, calculated by means of the formula $\dfrac{p_1+p_2}{\dfrac{p_1}{n_1}+\dfrac{p_2}{n_2}}$, in which p_1 and p_2 are the percentage weight of the liquids 1 and 2, n_1 and n_2 being their respective refractive indices; C_n the contraction undergone by the refractive power, calculated by means of the formula $\dfrac{n-n_v}{n}$; A the refraction constant, that is, the ratio $\dfrac{C_v}{C_n}$.)

Solution I.

$t = 11·9°$ *; $C_v = -1·162$.

	n.	n_v.	$n_v : n$.	C_n.	A.
r	1·57917	1·58942	1·00649	−0·649	*1·791*
D	1·58723	1·59775	1·00663	0·663	*1·753*
b	1·60856	1·61964	1·00689	0·689	*1·687*
v	—	—	—	—	—

$t = 23·1°$; $C_v = -1·212$.

r	1·57066	1·58133	1·00679	−0·679	*1·785*
D	1·57854	1·58952	1·00696	0·696	*1·742*
b	1·59962	1·61114	1·00720	0·720	*1·683*
v	1·61862	1·63055	1·00737	0·737	*1·645*

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* Solution not quite clear, and difficult to read at low temperatures.

Solution I. (continued).

$t = 44{\cdot}3^\circ$; $C_v = -1{\cdot}326$.

	n.	n_v.	$n_v : n$.	C_n.	*A.*
r	1·55416	1·56485	1·00688	−0·688	*1·928*
D	1·56172	1·57284	1·00711	0·711	*1·865*
b	1·58211	1·59362	1·00727	0·727	*1·823*
v	1·60047	1·61331	0·00740	0·740	*1·792*

Solution II.

$t = 13{\cdot}9^\circ$; $C_v = -2{\cdot}200$.

	n.	n_v.	$n_v : n$.	C_n.	*A.*
r	1·44279	1·45958	1·01164	−1·164	*1·890*
D	1·44695	1·46389	1·01171	1·171	*1·879*
b	1·45740	1·47501	1·01208	1·208	*1·821*
v	1·46636	1·48425	1·01220	1·220	*1·803*

$t = 21{\cdot}1^\circ$; $C_v = -2{\cdot}292$.

r	1·43875	1·45592	1·01193	−1·193	*1·921*
D	1·44281	1·46022	1·01207	1·207	*1·899*
b	1·45321	1·47122	1·01239	1·239	*1·850*
v	1·46211	1·48043	1·01253	1·253	*1·829*

$t = 35{\cdot}0^\circ$; $C_v = -2{\cdot}525$.

r	1·43065	1·44869	1·01261	−1·261	*2·003*
D	1·43461	1·45290	1·01275	1·275	*1·980*
b	1·44470	1·46372	1·01317	1·317	*1·917*
v	1·45340	1·47275	1·01331	1·331	*1·897*

Solution III.

$t = 11{\cdot}5^\circ$; $C_v = -1{\cdot}495$.

	n.	n_v.	$n_v : n$.	C_n.	*A.*
r	1·40555	1·41645	1·00775	−0·775	*1·929*
D	1·40855	1·41957	1·00782	0·782	*1·912*
b	1·41614	1·42737	1·00793	0·793	*1·885*
v	1·42215	1·43353	1·00800	0·800	*1·869*

$t = 23{\cdot}0^\circ$; $C_v = -1{\cdot}568$.

r	1·40011	1·41131	1·00799	−0·799	*1·962*
D	1·40300	1·41439	1·00812	0·812	*1·931*
b	1·41035	1·42211	1·00834	0·834	*1·880*
v	1·41617	1·42822	1·00851	0·851	*1·843*

$t = 41{\cdot}2^\circ$; $C_v = -1{\cdot}787$.

r	1·39132	1·40298	1·00835	−0·835	*2·140*
D	1·39424	1·40603	1·00846	0·846	*2·112*
b	1·40130	1·41357	1·00875	0·875	*2·042*
v	1·40698	1·41955	1·00893	0·893	*2·000*

For the same temperature and the same wave-length, the ratio $C_v/C_n = A$ is fairly constant, especially if we consider that the data for solution I. are less certain, owing to the proximity of a critical end-point and the difficulty of the determinations of refractive index. At higher temperature the value C_n increases as well as that of C_v; but the changes are not quite proportional, as appears from a slight increase of A. The same behaviour is to be observed for the other wave-lengths, but the absolute values of A diminish with the diminution of the wave-length. This is entirely in accordance with previous observations on mixtures with carbon disulphide; the theoretical meaning of the phenomenon has previously been discussed (*Bull. Acad. roy. Belg.*, 1912, 67).

iso*Butyric Acid + Carbon Disulphide.*

This system undergoes less dilatation than the former one.

Density of acid used: 0·96211 at 11·4°, 0·93921 at 34·2°, 0·91978 at 53·2°, and 0·89795 at 74·4°.

The solutions give:

I.—iso*Butyric Acid,* 20·336 *per cent.* + *Carbon Disulphide,* 79·664 *per cent.*

$t°$.	$d_{4°}^{t°}$.	d_v.	$d_v : d$.	C_v.
13·35°	1·18353	1·19433	1·00913	−0·913
22·7	1·17067	1·18166	1·00939	0·939
30·1	1·15993	1·17148	1·00999	0·999

II.—iso*Butyric Acid,* 45·276 *per cent.* + *Carbon Disulphide,* 54·724 *per cent.*

12·4°	1·09615	1·11078	1·01335	−1·335
21·1	1·08550	1·10011	1·01346	1·346
31·0	1·07236	1·08793	1·01452	1·452

III.—iso*Butyric Acid,* 68·028 *per cent.* + *Carbon Disulphide,* 31·972 *per cent.*

13·1°	1·03144	1·04242	1·01065	−1·065
20·4	1·02316	1·03421	1·01080	1·080
28·2	1·01398	1·02546	1·01133	1·133

The following are the results of the refraction determinations. For *iso*butyric acid:

$t°$.	r.	D.	b.	v.
9·05°	1·39491	1·39689	1·40170	1·40674
25·9	1·38782	1·38973	1·39446	1·39940
39·4	1·38210	1·38394	1·38860	1·39346
68·4	1·36967	1·37145	1·37598	1·38064

For the solutions:

Solution I.

$t = 11·75°$; $C_v = -0·909$.

	n.	n_v.	$n_v : n$.	C_n.	*A*.
r	1·55726	1·57173	1·00929	– 0·929	0·978
D	1·56445	1·57935	1·00952	0·952	0·955
b	1·58365	1·59928	1·00987	0·987	0·921
v	1·60070	1·61755	1·01053	1·053	0·863

$t = 19·5°$; $C_v = -0·930$.

r	1·55182	1·56644	1·00942	– 0·942	0·987
D	1·55908	1·57396	1·00954	0·954	0·975
b	1·57792	1·59370	1·01000	1·000	0·930
v	1·59495	1·61179	1·01057	1·057	0·880

$t = 34·5°$; $C_v = -1·029$.

r	1·54080	1·55538	1·00946	– 0·946	0·088
D	1·54810	1·56299	1·00962	0·962	1·069
b	1·56651	1·58245	1·01011	1·011	1·017
v	1·58325	1·60008	1·01063	1·063	0·968

Solution II.

$t = 11·2°$; $C_v = -1·333$.

	n.	n_v.	$n_v : n$.	C_n.	*A*.
r	1·49173	1·51165	1·01335	– 1·335	0·999
D	1·49687	1·51722	1·01359	1·359	0·981
b	1·51025	1·53160	1·01414	1·414	0·943
v	1·52292	1·54485	1·01440	1·440	0·926

$t = 18·2°$; $C_v = -1·342$.

r	1·48758	1·50748	1·01337	– 1·337	1·004
D	1·49253	1·51297	1·01370	1·370	0·980
b	1·50579	1·52726	1·01426	1·426	0·941
v	1·51835	1·54045	1·01455	1·455	0·923

$t = 30·8°$; $C_v = -1·450$.

r	1·47988	1·49997	1·01370	– 1·370	1·058
D	1·48470	1·50531	1·01388	1·388	1·045
b	1·49783	1·51929	1·01446	1·446	1·003
v	1·51000	1·53232	1·01478	1·478	0·981

Solution III.

$t = 13·2°$; $C_v = -1·065$.

	n.	n_v.	$n_v : n$.	C_n.	*A*.
r	1·44464	1·45936	1·01019	– 1·019	1·045
D	1·44813	1·46329	1·01047	1·047	1·017
b	1·45749	1·47330	1·01078	1·078	0·988
v	1·46663	1·48275	1·01099	1·099	0·969

Solution III. (continued).

$t = 18·45°$; $C_v = -1·176$.

	n.	n_v.	$n_v : n$.	C_n.	A.
r	1·44178	1·45668	1·01033	−1·033	*1·041*
D	1·44515	1·46060	1·01069	1·069	*1·007*
b	1·45460	1·47055	1·01097	1·097	*0·988*
v	1·46356	1·47995	1·01120	1·120	*0·961*

$t = 38·0°$; $C_v = -1·185$.

r	1·43136	1·44651	1·01058	−1·058	*1·120*
D	1·43480	1·45021	1·01074	1·074	*1·103*
b	1·44395	1·45990	1·01105	1·105	*1·072*
v	1·45274	1·46909	1·01126	1·126	*1·052*

In this system, which is more convenient for study than the former one, there is also more regularity in the A-values. The principal fact to notice is that the dilatation of the refraction is nearly of the same order as in the case of acetic acid-carbon disulphide mixtures; the density-dilatation, on the other hand, is much less; this appears clearly in the low value of the refraction constant (1 as compared with 1·9).

The other particulars, as, for instance, the increase of A with the temperature, are exactly as before, as is shown in the table.

iso*Valeric Acid* + *Carbon Disulphide.*

Density of the acid employed: 0·93319 at 17·6°, 0·91204 at 40·2°, and 0·89222 at 60·8°.

In this case also, three solutions were examined:

I.—iso*Valeric Acid,* 28·295 *per cent.* + *Carbon Disulphide,* 71·705 *per cent.*

$t°$.	$d^{t°}_{4°}$.	d_v.	$d_v : d$.	C_v.
12·15°	1·14718	1·15772	1·00919	−0·919
20·7	1·13613	1·14672	1·00932	0·932
30·7	1·12267	1·13366	1·00979	0·979

II.—iso*Valeric Acid,* 45·900 *per cent.* + *Carbon Disulphide,* 54·100 *per cent.*

14·2°	1·08096	1·09244	1·01062	−1·062
22·3	1·07130	1·08288	1·01081	1·081
31·2	1·06044	1·07249	1·01127	1·127

III.—iso*Valeric Acid,* 62·573 *per cent.* + *Carbon Disulphide,* 37·427 *per cent.*

10·2°	1·03281	1·04341	1·00928	−0·928
19·7	1·02326	1·03298	1·00950	0·950
30·7	1·01100	1·02102	1·00991	0·991

This again is a qualitative, if not quantitative, reproduction of the behaviour already observed for the previous systems.

The refractive index of *iso*valeric acid is:

$t°$.	r.	D.	b.	v.
8·1°	1·40524	1·40736	1·41231	1·41770
28·3	1·39684	1·39888	1·40369	1·40905
41·9	1·39121	1·39322	1·39830	1·40318
57·0	1·38499	1·38694	1·39185	1·39667

Solution I.

$t=9{\cdot}5°$; $C_v=-0{\cdot}916$.

	n.	n_v.	$n_v : n$.	C_n.	A.
r	1·53953	1·55659	1·01108	−1·108	*0·827*
D	1·54626	1·56392	1·01142	1·142	*0·802*
b	1·56353	1·58210	1·01188	1·188	*0·771*
v	1·57872	1·59880	1·01272	1·272	*0·720*

$t=20{\cdot}3°$; $C_v=-0{\cdot}931$.

r	1·53254	1·54978	1·01125	−1·125	*0·828*
D	1·53891	1·55668	1·01155	1·155	*0·806*
b	1·55571	1·57463	1·01216	1·216	*0·766*
v	1·57084	1·59122	1·01297	1·297	*0·718*

$t=32{\cdot}0°$; $C_v=-0{\cdot}985$.

r	1·52466	1·54202	1·01138	−1·138	*0·866*
D	1·53095	1·54873	1·01161	1·161	*0·849*
b	1·54755	1·56639	1·01217	1·217	*0·809*
v	1·56253	1·58270	1·01291	1·291	*0·763*

Solution II.

$t=8{\cdot}0°$; $C_v=-1{\cdot}049$.

	n.	n_v.	$n_v : n$.	C_n.	A.
r	1·49817	1·51748	1·01289	−1·289	*0·814*
D	1·50346	1·52309	1·01306	1·306	*0·803*
b	1·51683	1·53766	1·01372	1·372	*0·765*
v	1·52851	1·55107	1·01476	1·476	*0·712*

$t=19{\cdot}8°$; $C_v=-1{\cdot}073$.

r	1·49131	1·51046	1·01284	−1·284	*0·836*
D	1·49639	1·51600	1·01311	1·311	*0·818*
b	1·50947	1·53024	1·01376	1·376	*0·780*
v	1·52098	1·54348	1·01479	1·479	*0·726*

$t=26{\cdot}6°$; $C_v=-1{\cdot}102$.

r	1·48709	1·50641	1·01299	−1·299	*0·848*
D	1·49213	1·51185	1·01322	1·322	*0·833*
b	1·50509	1·52595	1·01386	1·386	*0·795*
v	1·51673	1·53922	1·01483	1·483	*0·743*

Solution III.

$t = 11{\cdot}2^{\circ}$; $C_v = -0{\cdot}929$.

	n.	n_v.	$n_v : n$.	C_n.	A.
r	1·46271	1·47929	1·01134	−1·134	0·819
D	1·46666	1·48372	1·01163	1·163	0·799
b	1·47695	1·49488	1·01214	1·214	0·765
v	1·48583	1·50552	1·01325	1·325	0·701

$t = 20{\cdot}5^{\circ}$; $C_v = -0{\cdot}951$.

	n.	n_v.	$n_v : n$.	C_n.	A.
r	1·45754	1·47436	1·01154	−1·154	0·824
D	1·46158	1·47872	1·01173	1·173	0·811
b	1·47161	1·48973	1·01231	1·231	0·773
v	1·48051	1·50035	1·01340	1·340	0·710

$t = 37{\cdot}7^{\circ}$; $C_v = -1{\cdot}030$.

	n.	n_v.	$n_v : n$.	C_n.	A.
r	1·44841	1·46516	1·01156	−1·156	0·890
D	1·45234	1·46940	1·01175	1·175	0·876
b	1·46210	1·48041	1·01252	1·252	0·823
v	1·47066	1·49051	1·01349	1·349	0·764

The value A is still less than in the case of *iso*butyric acid, but the diminution is only about 0·2. This seems to be in accordance with a previous observation on aqueous solutions: the differences in the value of A from one term to the other diminish gradually with the rise in an organic series. It would be interesting to investigate if propionic acid, coming between acetic and *iso*valeric acids, would give an intermediate value of A, about 1·4.

Besides these three acids, *iso*butyl alcohol was also examined in carbon disulphide solutions.

iso*Butyl Alcohol + Carbon Disulphide.*

Density of the pure alcohol: 0·80680 at 16·25°, 0·79423 at 31·8°, 0·77651 at 53·0°, and 0·75829 at 74·65°.

In the following table are the density values of the mixtures, showing that the dilatation increases with the temperature.

I.—iso*Butyl Alcohol*, 15·803 *per cent.* + *Carbon Disulphide*, 84·197 *per cent.*

t°.	d^t_4.	d_v.	$d_v : d$.	C_v.
11·3°	1·16304	1·16933	1·00541	−0·541
18·75	1·15392	1·16051	1·00571	0·571
31·7	1·13648	1·14341	1·00610	0·610

II.—iso*Butyl Alcohol*, 30·008 *per cent.* + *Carbon Disulphide*, 69·992 *per cent.*

$t°$.	$d_4^{t°}$.	d_v.	$d_v : d$.	C_v.
13·9°	1·07702	1·08516	1·00756	−0·756
21·1	1·06903	1·07718	1·00763	0·763
34·2	1·05245	1·06113	1·00825	0·825

III.—iso*Butyl Alcohol*, 50·220 *per cent.* + *Carbon Disulphide*, 49·780 *per cent.*

15·5°	0·97919	0·98637	1·00733	−0·733
30·7	0·96248	0·97032	1·00814	0·814

IV.—iso*Butyl Alcohol*, 70·388 *per cent.* + *Carbon Disulphide*, 29·612 *per cent.*

13·8°	0·90118	0·90668	1·00610	−0·610
32·4	0·88336	0·88919	1·00660	0·660

Refraction of iso*Butyl Alcohol.*

$t°$.	r.	D.	b.	v.
8·0°	1·39814	1·39996	1·40496	1·40885
23·7	1·39192	1·39372	1·39868	1·40248
34·9	1·38733	1·38912	1·39403	1·39779
49·1	1·38137	1·38311	1·38798	1·39169
66·3	1·37398	1·37568	1·38045	1·38463
86·0	1·36529	1·36686	1·37138	1·37506

The numbers for the four solutions are contained in the next table:

Solution I.

$t = 9·6°$; $C_v = -0·530$.

	n.	n_v.	$n_v : n$.	C_n.	A.
r	1·56877	1·58537	1·01058	−1·058	*0·501*
D	1·57631	1·59337	1·01082	1·082	*0·490*
b	1·59630	1·61452	1·01141	1·141	*0·465*
v	1·61402	1·63335	1·01198	1·198	*0·442*

$t = 28·9°$; $C_v = -0·601$.

r	1·55461	1·57158	1·01092	−1·092	*0·550*
D	1·56198	1·57943	1·01117	1·117	*0·538*
b	1·58130	1·59997	1·01181	1·181	*0·509*
v	1·59852	1·61849	1·01243	1·243	*0·483*

$t = 39·7°$; $C_v = -0·638$.

r	1·54632	1·56387	1·01135	−1·135	*0·562*
D	1·55357	1·57146	1·01152	1·152	*0·554*
b	1·57260	1·59170	1·01215	1·215	*0·525*
v	1·58963	1·60986	1·01273	1·273	*0·501*

Solution II.

$t=8{\cdot}3^\circ$; $C_v=-0{\cdot}728$.

	n.	n_v.	$n_v : n$.	C_n.	*A.*
r	1·52753	1·55104	1·01539	−1·539	*0·473*
D	1·53380	1·55780	1·01565	1·565	*0·462*
b	1·54994	1·57565	1·01659	1·659	*0·439*
v	1·56416	1·59132	1·01737	1·737	*0·413*

$t=25{\cdot}2^\circ$; $C_v=-0{\cdot}780$.

r	1·51660	1·54012	1·01551	−1·551	*0·503*
D	1·52266	1·54672	1·01580	1·580	*0·494*
b	1·53833	1·56426	1·01686	1·686	*0·463*
v	1·55212	1·57974	1·01779	1·779	*0·438*

$t=33{\cdot}6^\circ$; $C_v=-0{\cdot}822$.

r	1·51057	1·53445	1·01581	−1·581	*0·520*
D	1·51664	1·54104	1·01609	1·609	*0·511*
b	1·53216	1·55831	1·01707	1·707	*0·482*
v	1·54592	1·57364	1·01793	1·793	*0·459*

Solution III.

$t=11{\cdot}8^\circ$; $C_v=-0{\cdot}712$.

	n.	n_v.	$n_v : n$.	C_n.	*A.*
r	1·47802	1·50155	1·01592	−1·592	*0·447*
D	1·48276	1·50664	1·01611	1·611	*0·442*
b	1·49445	1·52015	1·01719	1·719	*0·415*
v	1·50484	1·53186	1·01796	1·796	*0·398*

$t=22{\cdot}1^\circ$; $C_v=-0{\cdot}770$.

r	1·47223	1·49580	1·01601	−1·601	*0·481*
D	1·47679	1·50078	1·01625	1·625	*0·474*
b	1·48884	1·51467	1·01735	1·735	*0·444*
v	1·49866	1·52576	1·01808	1·808	*0·426*

$t=34{\cdot}6^\circ$; $C_v=-0{\cdot}833$.

r	1·46497	1·48856	1·01610	−1·610	*0·517*
D	1·46938	1·49356	1·01646	1·646	*0·506*
b	1·48076	1·50661	1·01746	1·746	*0·477*
v	1·49083	1·51803	1·01825	1·825	*0·457*

Solution IV.

$t=9{\cdot}5^\circ$; $C_v=-0{\cdot}590$.

	n.	n_v.	$n_v : n$.	C_n.	*A.*
r	1·44132	1·45834	1·01181	−1·181	*0·500*
D	1·44470	1·46201	1·01198	1·198	*0·492*
b	1·45326	1·47161	1·01263	1·263	*0·467*
v	1·46068	1·47999	1·01322	1·322	*0·446*

Solution IV. (continued).

$t=22{\cdot}4^\circ$; $C_v=-0{\cdot}636$.

	n.	n_v.	$n_v : n$.	C_n.	A.
r	1·43506	1·45222	1·01196	−1·196	*0·532*
D	1·43825	1·45565	1·01210	1·210	*0·521*
b	1·44665	1·46529	1·01288	1·288	*0·458*
v	1·45366	1·47345	1·01361	1·361	*0·433*

$t=28{\cdot}8^\circ$; $C_v=-0{\cdot}651$.

	n.	n_v.	$n_v : n$.	C_n.	A.
r	1·43172	1·44877	1·01198	−1·198	*0·543*
D	1·43496	1·45239	1·01214	1·214	*0·536*
b	1·44320	1·46197	1·01300	1·300	*0·508*
v	1·45015	1·47009	1·01375	1·375	*0·474*

The first point is that the value of A (0·47 at about 10° for the *D*-ray) is less, but only very slightly so, than that found for the mixtures of carbon disulphide in ethyl alcohol; I showed that the latter, according to the experiments of Wüllner and of Zecchini (*Bull. Acad. roy. Belg.*, 1912, 57)—reduced to the same temperature—does not exceed 0·52. The difference is much less than that between two terms of the fatty acid series.

Another important point is that the refraction constant is only half that of the corresponding acid; on the other hand, I showed previously that in the case of aqueous solutions, the figures for A are of the same order, both for acids and alcohols, and the difference, if any, is in the opposite sense. The numbers were (*Mem. Acad. roy. Belg.*, 1911, 17): ethyl alcohol + water, A = 3·36, and acetic acid + water, A = 3·1 (for concentrated, that is, non-dissociated solutions); *iso*butyl alcohol + water, A = 2·65, and *iso*butyric acid + water, A = 2·6. Further, we know that in aqueous solutions the A-value of acetone is 3·45, almost the same as for ethyl alcohol; with carbon disulphide solutions the value for acetone (= 0·72) (*Bull. Acad. roy. Belg.*, 1912, 61) and for ethyl alcohol (= 0·52) have a marked difference.

This shows once more that the refraction constant is, above all, a characteristic value for each system, depending on constitutive influences; in spite of the regularities I have been able to deduce up to now, it would be premature to draw too rapid conclusions before extending still much further the experimental researches.

As was mentioned in the introduction, the use of carbon disulphide as a solvent opens up a large field, and one easy of exploration. Want of time has prevented me from examining other mixtures; as I am not certain that I may be able to continue the problem soon, I decided to publish the results given by the study of the four systems studied in the present paper. As has been shown, some new conclusions may be drawn, which may be summarised briefly as follows:

(*A*) In mixture with carbon disulphide, organic liquids (acids, alcohols) differ from the corresponding aqueous solutions in the following points:

(1) The values observed for the density and refraction are less than the theoretical values; the mixtures thus undergo a dilatation, and not a contraction, as is generally the case for aqueous solutions.

(2) The values $C_v/C_n = A$ (refraction constant) are much less than for the corresponding solutions in water.

(3) Moreover, there is no regular proportionality between the *A*-values in water and in carbon disulphide, which shows how much *A* is determined by constitutive influences.

(*B*) In spite of these differences, carbon disulphide solutions have several properties in common with aqueous solutions:

(1) If we examine the solutions of carbon disulphide successively with the different terms of a series, the value of *A* diminishes with the increase of the molecular weight.

(2) Increase of temperature produces increase of *A*.

(3) The refraction constant diminishes from the red to the violet of the spectrum.

LONDON AND LIÉGE.

CCI.—*Studies of Dynamic Isomerism. Part XIII. Camphorcarboxylamide and Camphorcarboxypiperidide. An Illustration of Barlow and Pope's Hypothesis.*

By WALTER HAMIS GLOVER and THOMAS MARTIN LOWRY.

1. *Esters of Camphorcarboxylic Acid.*

Of all the derivatives of camphor in which reversible isomeric change is possible, the esters of camphorcarboxylic acid are those which approach most nearly to the classical case of ethyl acetoacetate. Unfortunately, all the esters that have been prepared up to the present are liquids, in which the various isomerides are probably mixed together in much the same way as when equilibrium is attained in solution. In such cases the addition of a solvent may cause a small displacement of the equilibrium, and thus produce some alteration in the rotatory power of a freshly prepared solution. The large changes of rotatory power and of solubility, which are observed after dissolving homogeneous solids such as α-glucose or normal nitrocamphor, cannot, however, be expected in the case of a liquid mixture in which a condition of equilibrium already exists. Small changes of rotatory power, similar to those produced by dissolution, may also result from the distillation of the liquid esters.

The smallness of the displacement of equilibrium in the case of liquids may be illustrated by the following observations on the effect of distilling methyl camphorcarboxylate. The observed rotations for a 2-dcm. column of the ester for wave-length 5461 were:

Original ester	161·84°	After 36 days	161·01°
After distilling	160·87	,, 114 ,,	161·11
,, 1 day	160·87	,, 439 ,,	161·22
,, 8 days	160·96		

The change of rotatory power produced by the distillation amounts only to 1 part in 160, and but for the large value of the observed rotation (nearly two right angles) would almost certainly have escaped detection. The subsequent rise of rotatory power is so slow as to suggest the possibility that it might be due to some decomposition of the ester by oxidation or hydrolysis, but a number of analogous cases are known in which the velocity of change is even slower, an extreme case being that of α-bromocamphor, which does not change at all unless alkali is added; we believe therefore that the alterations of rotatory power recorded above are a direct result of a displacement, during the distillation, of the equilibrium between the various isomeric forms of the ester, followed by a slow reversion to the original condition.

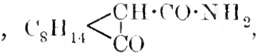
Several attempts were made in the course of the investigation to prepare a crystalline ester by condensing the silver salt of camphorcarboxylic acid with benzyl and with cetyl iodides, but in no case was a crystalline product obtained. This negative result may be due in part to the fact that the liquid esters probably contain not less than three isomerides in equilibrium, and may therefore persist, as viscous oils, at temperatures much below those at which the various isomerides would crystallise if they could be prepared separately. The acid, which crystallises very readily, appears to be homogeneous, and has no tendency to undergo isomeric change.

The acid was prepared with the help of sodamide, as described by Brühl (*Ber.*, 1903, **36**, 1306). If care is taken to powder the sodamide ($\frac{1}{4}$ lb.) finely under benzene, and to digest it for a couple of hours with camphor ($\frac{1}{2}$ lb.) and benzene ($1\frac{1}{2}$ litres) in a flask provided with a stirrer and condenser, we find that on passing in carbon dioxide from a cylinder, the whole solidifies to a gelatinous mass, and a good yield of acid is obtained. The mixture is, however, extremely inflammable, and again and again we have had to deal with cases of ignition on bringing the mixture into contact with water. The inflammability appears to be due to tiny fragments of sodamide (possibly containing a little sodium[*]), which become encased by the gelatinous sodium salt and so escape the action of the carbon dioxide, but become exposed again when the sodium salt is acted on by water. If the gelatinous salt is raked out into a basin and transferred into iced water in an earthenware jar (provided with a cover to act as an extinguisher), the bulk of the product can be decomposed safely, as the salt with the enclosed sodamide floats between the water and benzene and is not exposed to the air; but tiny conflagrations frequently occur on washing out the flask, or on filtering the mixture of benzene and water, if the decomposition is not quite complete.

The product can be purified very effectively by fractional precipitation of the acid. The first additions of mineral acid to the alkaline solution cause the precipitation of a brown resin. If this precipitation is carried to the point at which a little of the acid is thrown down, the remainder can be separated in a very pure state from the filtered solution; the small fraction of impure acid can be redissolved in sodium carbonate and reprecipitated cautiously in order to free it from resin. This method of purification is very convenient, and is at least as efficient as crystallisation from benzene, which need only be resorted to when a dry, crystalline acid is required.

It is of interest to notice that the methyl ester, which usually has a slight colour, can be bleached completely by exposure to sunlight, even in the case of the yellow samples prepared from crude acid.

2. *Camphorcarboxylamide.*

Camphorcarboxylamide,  $C_8H_{14}<\begin{matrix}CH\cdot CO\cdot NH_2\\ |\\ CO\end{matrix}$, unlike the esters, is a crystalline compound, and has afforded very valuable material for the study of isomeric change. It is prepared by the action of ammonia on an ester of camphorcarboxylic acid, and is most readily obtained in the following manner: 20 grams of methyl camphorcarboxylate are shaken with 60 to 70 c.c. of concentrated ammonia in a sealed tube for several hours, until the ester assumes

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[*] All samples of sodamide do not appear to be equally dangerous.

a gelatinous, opaque appearance; the tube and its contents are then heated at 100° for seven hours, after which the contents of the tube, consisting of a pale brown, viscid oil and an aqueous layer, are transferred to an evaporating dish and heated on a water-bath until the water and most of the camphor (formed by hydrolysis of the ester and decomposition of the resulting acid) are driven off; the brown, viscid residue is cooled by placing the basin on ice, and is then covered with light petroleum; on stirring the mixture, the amide separates as a white, crystalline powder, which can be freed from the last traces of camphor by filtering and washing with light petroleum, in which the amide is only sparingly soluble; the crude amide obtained in this way is purified by crystallising from benzene and from light petroleum.

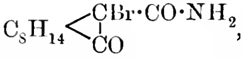
The amide separates from petroleum in glistening, pearly scales. By slow evaporation of a solution in benzene, compact, tabular crystals are produced, but these become opaque in the course of a few minutes; this change is not accompanied by any marked decrease in weight, so cannot be attributed to the escape of benzene of crystallisation; it is very probable that the substance is dimorphous, and that the opacity is due to the disintegration of the original crystals, but we have not been able to obtain any more definite evidence of this. By slow evaporation of a solution in ethyl acetate, well-developed crystals were obtained, which remained transparent and gave a very satisfactory series of measurements.

The amide is soluble in hot water and in all the common organic solvents; an aqueous solution gives a beautiful indigo-blue coloration with ferric chloride, changing to green on keeping or when the solution is warmed:

0·1990 gave 12·6 c.c. N_2 (dry) at 18·5° and 749 mm. N = 7·33.
0·2120 „ 13·3 c.c. N_2 „ „ 16° and 758 mm. N = 7·41.
$C_{11}H_{17}O_2N$ requires N = 7·18 per cent.

As in the case of many other substances which undergo isomeric change, the melting point of the amide is very variable, depending both on the rate of heating and on the previous treatment of the crystalline material. The well-formed crystals which separate from ethyl acetate do not melt at once when suddenly heated to 120°, and it is possible that the true melting point of the unchanged amide may lie even a degree or two above this temperature. The small spangles which separate from light petroleum, or by rapid crystallisation from benzene, are not homogeneous, and may melt at any temperature from 112° to 118°. The fused substance, when allowed to crystallise by cooling (it does not always crystallise), remelts sharply at 96—97° if heated in a bath from 60°. The last melting point probably represents the "equilibrium temperature" (Trans., 1899, **75**, 233; *Brit. Assoc. Report*, 1904, p. 217) at which the solid amide is in equilibrium with a fused mixture of the various isomerides in their normal proportions.

The rotatory power of the amide is also very variable. The value finally attained in alcoholic solutions of the amide is $[\alpha]_{5461}+100°$, whilst in benzene the value is $[\alpha]_{5461}+75°$. The initial rotatory power of the freshly prepared solutions varies according to the method of crystallisation. Various samples crystallised from light petroleum and dissolved in alcohol gave values ranging from $[\alpha]_{5461}+8°$ to 53°, 57°, and 71°, whilst in the case of some of the samples the maximum value of 100° was already observed in the initial readings taken within an hour of the time when the solution was prepared. Definite values for the initial rotatory power were only obtained after the method had been discovered of preparing well-formed crystals of the amide by slow evaporation of solutions in ethyl acetate or in benzene. Crystals which had separated from ethyl acetate gave $[\alpha]_{5461}-0{\cdot}2°$ when dissolved in alcohol, and $+1{\cdot}5°$ when dissolved in benzene; well-formed crystals which had separated from benzene gave $[\alpha]_{5461}+2{\cdot}2°$ when dissolved in alcohol; a crop of crystals which had been obtained by allowing the benzene to evaporate to dryness gave $[\alpha]_{5461}+5°$ in benzene and +8° in alcohol, but these were evidently less pure. From these observations it is clear that the stable form of the amide, the crystalline constants of which are given later, is almost inactive, its specific rotatory power lying within a degree or two on one side or other of the zero, but that in solution it readily passes over into isomerides which are strongly dextrorotatory.



$\alpha\alpha'$-Bromocamphorcarboxylamide, $C_8H_{14}{<}\genfrac{}{}{0pt}{}{CBr\cdot CO\cdot NH_2}{CO}$, is prepared by acting on a solution of the amide in glacial acetic acid with an equivalent quantity of bromine at the ordinary temperature. The solution is allowed to remain for several hours, poured into water, the white precipitate collected, dried, and crystallised from light petroleum or alcohol. The bromo-amide separates from light petroleum in granules, and from alcohol in colourless, glistening, stout needles. It melts at 114°, and does not give a coloration with ferric chloride:

0·1832 gave 0·1258 AgBr. Br = 29·22.

$C_{11}H_{16}O_2NBr$ requires Br = 29·16 per cent.

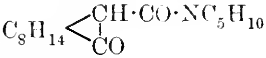
Unlike the parent substance, the bromo-amide does not exhibit mutarotation, either alone or in presence of an alkaline catalyst; after a few days, the alcoholic solution shows signs of decomposition and darkens in colour, but the decrease of rotatory power which then results is easily distinguished as of different origin from the more rapid changes observed in the parent amide. The rotatory powers for an alcoholic solution, containing 5 grams of the bromo-amide in 100 c.c., were as follows:

Wave-length	Li_{6708}	Na_{5893}	Hg_{5461}	Hg_{4359}
Specific rotation	+29·4°	+38·4°	+45·8°	+82·6°
Ratio to 5461	0·646	0·844	—	1·810

The figures for Hg_{5461} were constant over a period of twenty-four hours in a glass tube, and over a period of seventeen hours in a tube with disks cemented with "seccotine."

The *acetyl* derivative of the amide, prepared by boiling it for an hour with acetic anhydride, crystallises from alcohol, acetic acid, or ethyl acetate in flat needles, melts at 124°, and gives no coloration with ferric chloride. Its optical activity, like that of the amide, is very small, the specific rotatory power of a solution in benzene (2 grams per 100 c.c.) being only $[\alpha]_{5461} - 0·5°$ for the green mercury light; identical values were observed after fourteen and after twenty-four hours, and there is therefore no evidence that the substance can give rise to mutarotation phenomena. Its absorption spectrum is very similar to that of the amide, suggesting that it is derived from the amide by changing $\cdot NH_2$ into $\cdot NH\cdot CO\cdot CH_3$, and is not an enolic acetate.

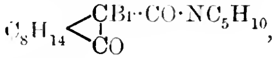
3. *Camphorcarboxypiperidide.*

Camphorcarboxypiperidide,  $C_8H_{14}<\begin{matrix}CH\cdot CO\cdot NC_5H_{10}\\ | \\ CO\end{matrix}$, is readily prepared by heating molecular proportions of piperidine and of methyl camphorcarboxylate in a stoppered bottle for five hours; the viscid product solidifies when cold to a crystalline mass, and may be purified by crystallising from alcohol and then from light petroleum. Large, well-developed, measurable crystals are obtained by the slow evaporation of a solution in ethyl acetate.

Unlike the amide, which only yields a homogeneous product when crystallised under somewhat special conditions, the piperidide requires no special treatment in order to secure substantial uniformity; but the use of ethyl acetate as solvent was found to be advantageous in producing well-formed crystals of undoubted purity. The melting point of the piperidide is 104°, but it can also be melted by longer heating at lower temperatures down to about 98°; the melted piperidide does not usually crystallise when cooled, and the "equilibrium temperature" (of the solid piperidide in contact with a fusion of normal composition) was therefore not determined. The rotatory power of the piperidide in freshly prepared solutions is also far more definite than in the case of the amide, the initial values for three samples being $[\alpha]_{5461}+24{\cdot}3^\circ$, $25{\cdot}8^\circ$, and $24{\cdot}6^\circ$, mean $24{\cdot}9^\circ$, when dissolved in benzene, whilst three samples dissolved in alcohol gave $[\alpha]_{5461}+109^\circ$, 112°, and 112°, mean 111°.

The piperidide resembles the amide in giving a coloration with ferric chloride, but the action is less pronounced, the alcoholic solution giving, on the addition of aqueous ferric chloride, only a dull, bluish-green colour in place of the fine indigo colour produced by the amide:

$0{\cdot}4539$ gave $1{\cdot}2142$ CO_2 and $0{\cdot}3907$ H_2O. $C=72{\cdot}94$; $H=9{\cdot}56$.
$C_{16}H_{25}O_2N$ requires $C=73{\cdot}00$; $H=9{\cdot}50$ per cent.

The *bromo-piperidide*,  $C_8H_{14}{<}\begin{array}{l}CBr\cdot CO\cdot NC_5H_{10}\\ \vert \\ CO\end{array}$, prepared in the same way as the bromo-amide, crystallises from alcohol in tufts of colourless, glistening, prismatic needles, melts at 132°, and does not give a coloration with ferric chloride. Like the bromo-amide, the substance decomposes and darkens in colour when its alcoholic solutions are kept for several days, but it does not exhibit mutarotation, the initial rotatory power observed after three minutes being unchanged after three hours, and again after twenty-four hours. Its specific rotatory power in alcoholic solution was observed to be as follows:

	Li_{6708}	Cd_{6438}	Na_{5893}	Hg_{5461}	Cd_{5086}	Cd_{4800}	Cd_{4678}	Hg_{4359}
$[\alpha]$	$-54{\cdot}5^\circ$	$-58{\cdot}5^\circ$	$-71{\cdot}2^\circ$	$-86{\cdot}0^\circ$	$-102{\cdot}3^\circ$	$-118{\cdot}0^\circ$	$-126{\cdot}0^\circ$	$-150{\cdot}9^\circ$
Ratio to $[\alpha]_{5461}$	0·634	0·680	0·829	1·000	1·190	1·372	1·465	1·755

$0{\cdot}278$ gave $0{\cdot}1526$ AgBr. $Br=23{\cdot}36$.
$C_{16}H_{24}O_2NBr$ requires $Br=23{\cdot}38$ per cent.

4. *Crystallographic Measurements.*

The crystals of camphorcarboxylamide (Fig. 1) which separate from ethyl acetate were found to have the following properties:

System. Monosymmetric.
Axial Ratios. $a:b:c=1{\cdot}4736:1:1{\cdot}7683$; $\beta=61^\circ2'$.
Forms Present. $c\{001\}$, $r\{110\}$, $p\{101\}$.

Angles Measured.

Angles.	No.	Limits.	Mean.	Calculated.
cr 001 : 110	14	72°28′ — 73°15′	72°44′	72°44′
cr $00\bar{1}$: 110	17	106 57 —107 30	107 16	—
rr 110 : $1\bar{1}0$	6	104 9 —104 45	104 23	104 25
rr 110 : $\bar{1}10$	8	75 22 — 75 47	75 35	—
cp 001 : $\bar{1}01$	6	67 51 — 68 35	68 15	—
pr $10\bar{1}$: 110	5	67 2 — 67 23	67 15	67 10

Crystals of the piperidide (Fig. 2), separated from ethyl acetate, gave the following data:

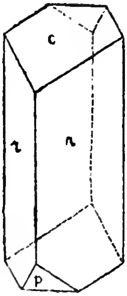
System. Hemihedral orthorhombic.

Axial Ratios. $a:b:c = 1{\cdot}5032:1:2{\cdot}4320$.

Forms Present. $b\{010\}$, $p\{011\}$, $o\{111\}$.

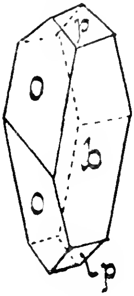
Habit. Flat hexagonal plates with the pinacoids {010} well developed.

FIG. 1.



Camphorcarboxylamide.

FIG. 2.



Camphorcarboxypiperidide.

Angles Measured.

Angles.	No.	Limits.	Mean.	Calculated.
bo 010 : 111	11	72°10′ — 72°28′	72°16′	—
bo 010 : $\bar{1}1\bar{1}$	11	107 29 —107 51	107 42	107°44′
bp 010 : 011	18	58 29 — 58 57	58 42	—
pp 011 : $0\bar{1}1$	9	62 15 — 62 46	62 26	62 36
op 111 : 011	5	53 57 — 54 23	54 7	54 6
oo 111 : $\bar{1}1\bar{1}$	3	71 38 — 71 50	71 45	71 48
op 111 : 011	2	74 13 — 74 27	74 20	74 22
op 111 : $0\bar{1}1$	1	105°38′	105 38	105 38

It is noteworthy that the piperidide, unlike sodium chlorate, develops only one of the two enantiomorphous forms which are possible in view of the "asymmetric" character of the system to which the crystals belong. Fourteen crystals were examined, all of which showed faces of the hemihedral form $o\{111\}$, but in no cases were faces of the opposite form $o\{\bar{1}11\}$ developed. This constancy in the sign of the hemihedrism is characteristic of crystals which owe their asymmetry to the structure, and not to the marshalling, of the molecules.

5. *Morphotropic Relationships.*

On comparing the axial ratios of the amide and piperidide, it is clear that the *c*-axis is the one that is most affected by the replacement of $\cdot NH_2$ by $\cdot NC_5H_{10}$. This view is also confirmed by a study of the equivalence parameters:

	Valency volume.	Axial ratios.		Equivalence parameters.
$C_{10}H_{15}O\cdot CO\cdot NH_2$ ...	68	1·4736 : 1 : 1·7683	$\beta=61^\circ 2'$	4·570 : 3·101 : 5·484
$C_{10}H_{15}O\cdot CO\cdot NC_5H_{10}$	94	1·5032 : 1 : 2·4320		4·469 : 2·973 : 7·230

The distortion produced by the addition of C_5H_8 amounts to 2 per cent. on the $a:b$ ratio, 2½ per cent. on the a-parameter, and 4 per cent. on the b-parameter, whilst the c-parameter is increased by not less than 30 per cent. The main effects of the introduction of the piperidyl group are (1) to destroy the obliquity of the crystal by changing β from 61° to 90°, (2) to add to the rectangular crystal thus produced an additional block whereby the height of the crystal is increased by 30 per cent.

An even more remarkable relationship exists between the amide and one of the two isomeric benzoylcamphors prepared by Forster and measured by Pope (Trans., 1910, **79**, 995 and 998). Both isomerides crystallise in the orthorhombic system, and show, as regards the values for one axial ratio, a close relationship, which becomes even more obvious if in each crystal the axis of intermediate length is selected as the b-axis, thus:

	Valency volume.	Axial ratios.	Equivalence parameters.
Enolic benzoylcamphor	92	0·6733 : 1 : 1·0280	3·436 : 5·103 : 5·246
Ketonic ,, ...	92	0·7375 : 1 : 1·0224	3·658 : 4·960 : 5·071

The c to b ratios agree within 0·5 per cent., but, in spite of the identity of the two substances as regards molecular weight and formula, the equivalence parameters differ by 5, 3, and 3 per cent. respectively.

It is therefore all the more remarkable that, when the axial ratios of the amide are brought to comparable form by doubling the length of the b-axis, the amide and the ketonic form of benzoylcamphor should exhibit the close relationship shown by the figures in heavy type in the following table:

	Valency volume.	Axial ratios.		Equivalence parameters.
$C_{10}H_{15}O\cdot CO\cdot NH_2$ ...	68	**0·7368 : 1 : 0·8841**	$\beta=61^\circ 2'$	**3·627 : 4·923 : 4·352**
$C_{10}H_{15}O\cdot CO\cdot C_6H_5$ ...	92	**0·7375 : 1 : 1·0224**		**3·658 : 4·960 : 5·071**

Not only do the values for the ratio $a:b$ agree within 1 part in 1000, but the values for the a and b parameters agree within 0·8 per cent. The replacement of $\cdot NH_2$ by $\cdot C_6H_5$ has the effect of destroying the obliquity of the crystal, and adding to the rectangular crystal a block which increases its height by 16 per cent.; but the maximum distortion produced by this somewhat complex change amounts only to 0·8 per cent.

An analogous case in the camphor series is found in the comparison of camphoric anhydride with the molecular compound of camphoric acid and acetone (Barlow and Pope, Trans., 1906, **89**, 1685):

	Valency volume.	Axial ratios.	Equivalence parameters.
$C_{10}H_{14}O_3$	60	1·0011 : 1 : 1·7270	3·2654 : 3·2618 : 5·6331
$C_{10}H_{16}O_4,\frac{1}{2}(CH_3)_2CO$.	74	1·2386 : 1 : 1·7172	4·0435 : 3·2646 : 5·6060

in which the additional molecule of water and half-molecule of acetone go to increase the *a*-parameter only, the *b*- and *c*-parameters being increased only by 0·09 and 0·05 per cent. respectively. The case now described is, however, complicated by the fact that the addition to the length of the *c*-parameter is made only after the inclination β of the *a*- and *c*-axes has been increased from 61° to 90°.

It may perhaps be permitted to explain briefly the significance of these relationships as developed by the hypothesis of Barlow and Pope. The most casual inspection shows an equality in the *c* : *b* axial ratios of the crystals of camphoric anhydride and the camphoric acid compound, or between the *a* : *b* axial ratios of camphorcarboxylamide and ketonic benzoylcamphor. Such morphotropic relationships are immediately obvious, and, like the phenomena of isomorphism, do not require any further calculation to reveal them. The attempt to develop further regularities is, however, somewhat dangerous. For if the volume of the crystal-units be increased so as to be proportional to the molecular weight or molecular volume of the compound or to the number of atoms that it contains, the multiplying factor will usually be different for the two compounds that are being compared, and a series of figures will be obtained which show no obvious relationship to one another. Thus, in the case of the isomorphous sulphates of potassium and rubidium, we have:

	Mol. vol.	Axial ratios.		Topic axial ratios.
K_2SO_4	64·91	0·5727 : 1 : 0·7418	=	3·062 : 5·346 : 3·966
Rb_2SO_4	84·58	0·5712 : 1 : 0·7531	=	3·321 : 5·815 : 4·379

The choice of an unsuitable quantity has had the effect of disguising the regularity that was previously obvious, and no new regularity has made its appearance. In order that the old regularities may be maintained and new regularities developed, it is essential that the quantity or property chosen shall be proportional to the product $a \times b \times c$ of the axial ratios, or in the case of inclined crystals to the product $abc \sin\alpha \sin\beta \sin\gamma$. The significance, then, of Barlow and Pope's observations on camphoric anhydride and the compound of camphoric acid with acetone consists mainly in the fact that the ratio 2·127 : 1·729 = 1·230 of the axial products *abc* is practically identical with the ratio 74 : 60 = 1·233 of the sums of the valencies. In the case now under consideration this relationship does not hold good, the ratio 0·754 : 0·651 = 1·158 of the axial products being widely different from the ratio 92 : 68 = 1·353 of the sums of the valencies; but when the inclination of the *c*- and *a*-axes is taken into account, the ratio 0·754 : 0·573 = 1·323 of the products $abc \sin \beta$ agrees quite closely with the ratio of the sums of the valencies. It is for this reason that, when the volumes of the crystal-units are increased to correspond with the valency volumes, the old equality is maintained in the *a*-parameters, whilst in the *b*-parameters a new pair of equal numbers appears as evidence of the fertility of the hypothesis.

5. *Summary and Conclusions.*

1. Small changes of rotatory power are observed in freshly distilled methyl camphorcarboxylate. These are analogous with the changes of density noticed by Schaum in ethyl acetoacetate, and are attributed to isomeric change.

2. A crystalline amide and piperidide of camphorcarboxylic acid are described, which undergo isomeric change in solution, but yield fixed bromo-derivatives and, in the case of the amide, a fixed acetyl derivative.

3. The amide, when pure and homogeneous, is almost inactive, but its solutions develop a strong dextrorotation.

4. The piperidide is dextrorotatory, but its solutions show a marked increase of rotatory power when kept.

5. Both substances have been prepared in measurable crystals, those of the amide being monosymmetric, and those of the piperidide being orthorhombic in their symmetry.

6. By applying Barlow and Pope's hypothesis, a remarkable morphotropic relationship has been found between the monosymmetric crystals of camphorcarboxylamide and the orthorhombic crystals of the ketonic form of Forster's α-benzoylcamphor.

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CCII.—*Some New Diazoamino- and* o-*Aminoazo-compounds.*

By George Marshall Norman.

In the course of some experiments on diazoamino-compounds several new *o*-aminoazo-compounds have been obtained. Although no fresh evidence has been forthcoming as to the constitution of these substances, a few interesting facts in connexion with their formation are worth recording.

In the benzene series, the best-known compound of this kind is *o*-aminoazo-*p*-toluene, which has been the subject of several researches. Similar compounds have been obtained from the xylidines (Nölting and Forel, *Ber.*, 1885, **18**, 2682), but examples containing halogen or other radicles have not hitherto been described. Meldola (Trans., 1886, **49**, 631) records an unsuccessful attempt to obtain an aminoazo-derivative from *p*-nitrodiazoaminobenzene by fusing it with *p*-nitroaniline and its hydrochloride, but the failure may have been due to the high temperature necessary to obtain a molten mass.

It has been found possible to obtain an extremely small yield of an *o*-azo-compound from both 4 : 4′-dichlorodiazoaminobenzene and 4 : 4′-dibromodiazoaminobenzene by fusing these substances with the corresponding amine and its hydrochloride, and heating for twelve hours at 60—65°, but the chief product is a tarry, uncrystallisable solid. No doubt there is a great deal of decomposition, and on account of the poor yield a complete investigation of these substances has not yet been carried out.

In the naphthalene series the azo-derivatives of β-naphthylamine are produced without difficulty by the direct combination of the diazotised amine with β-naphthylamine, and those derived from aniline, *p*-toluidine, *p*-chloroaniline, *p*-bromoaniline, and the nitroanilines have been previously investigated. Some other examples are described later.

Experiments have also been carried out with some of the diazoamino-compounds obtained by coupling β-naphthalenediazonium chloride with the amines of the benzene series. These substances are produced easily with *p*-chloroaniline, *p*-bromoaniline, and *p*-toluidine. With *m*-toluidine a peculiar result is obtained; a tarry mass is formed which does not change on keeping, but alcohol causes the separation of a yellow solid, which proved to be the diazoamino-compound, apparently by dissolving the tarry, uncrystallisable substance. The yield was poor.

In the case of *o*-toluidine, a tarry mass was obtained, which was washed and allowed to remain overnight. It had changed next morning into a brown solid, which was identified as *o*-tolueneazo-β-naphthylamine. In this case, either there is an immediate interchange of the diazo- and amino-radicles, which would leave toluenediazonium chloride to react with β-naphthylamine, or the diazoamino-compound is formed first, and being unstable is transformed quickly into the azo-derivative. It is even possible that this diazoamino-compound is present in the tar which separates first, and changes slowly, in the probable presence of traces of acid. The diazoamino-compound obtained by the action of diazotised β-naphthylamine on *p*-toluidine certainly undergoes this change readily, for when heated with *p*-toluidine and its hydrochloride it gives *p*-tolueneazo-β-naphthylamine, whereas all recorded results show that mixed diazoamino-compounds containing the *p*-toluene residue with another substituted benzene nucleus, when heated with *p*-toluidine in this way, yield first diazoamino-*p*-toluene, and then the isomeric *o*-azo-derivative (Goldschmidt and Bardach, *Ber.*, 1892, **25**, 1347).

The diazoamino-compound may be decomposed by the acid into *p*-toluenediazonium chloride and β-naphthylamine, which would combine at once to form the aminoazo-compound. A similar change does not occur when the unsymmetrical diazoamino-compounds derived from β-naphthylamine and either *p*-chloroaniline or *p*-bromoaniline are heated with *p*-chloroaniline and *p*-bromoaniline respectively. The products are tarry, and although nothing could be separated, it seems possible that the same substances are formed as in the similar treatment of 4 : 4′-dichlorodiazoaminobenzene and 4 : 4′-dibromodiazoaminobenzene.

The results are all in agreement with the formulæ assigned to these compounds from their action on phenylcarbimide, namely,

$$C_6H_4Me{\cdot}N_2{\cdot}NH{\cdot}C_{10}H_7,\ C_6H_4Cl{\cdot}NH{\cdot}N_2{\cdot}C_{10}H_7,\ \text{and}$$
$$C_6H_4Br{\cdot}NH{\cdot}N_2{\cdot}C_{10}H_7,$$

and it has been proved that, when the compounds are heated with β-naphthol, the azo-derivatives formed contain the *p*-toluene nucleus in the first case, but the β-naphthalene nucleus in the other two.

There are, however, many difficulties in the way of the simple explanation that in the transformation of a diazoamino-compound it is decomposed into diazonium salt and amine, and that recombination then takes place. It has been shown by Goldschmidt, for instance, that the acid employed influences the result; diazoaminobenzene, when heated with dimethylaniline in the presence of hydrochloric acid, gives benzeneazodimethylaniline, but in the presence of weak organic acids, such as benzoic acid, it yields aminoazobenzene (*Ber.*, 1896, **29**, 1905).

These results indicate a probable intramolecular change, and it is possible that diazoamino-compounds can assume a quinonoid structure of type:

which would explain the readiness with which they pass into aminoazo-compounds. With the unsymmetrical compounds obtained from β-naphthylamine in particular, this formula would account for the ready transformation in the case of the *o*-toluidine and *p*-toluidine compounds, giving the azimino-structure to the resulting azo-derivatives.

Thus

In the case of the compounds derived from *p*-chloroaniline and *p*-bromoaniline, the quinonoid structure may appear in the benzene nucleus, so that the same ready transformation does not occur.

It is not urged, with the evidence available, that the solid diazoamino-compounds have this structure necessarily, but that such a substance may be formed under the influence of acids.

During the progress of this research experiments have been carried out on the action of nitrous acid, in the presence of warm acetic acid, on the *o*-azo-compounds prepared, showing that most probably the acetyl derivative of the corresponding hydroxyazo-compound is produced first, as discovered by Meldola and East (Trans., 1888, **53**, 465) in the case of the nitrobenzeneazo-β-naphthylamines.

EXPERIMENTAL.

4:4′-*Dibromo-2-aminoazobenzene*, $C_6H_4Br\cdot N_2\cdot C_6H_3Br\cdot NH_2$.

Thirty grams of 4:4′-dibromodiazoaminobenzene were dissolved in 120 grams of *p*-bromoaniline with 18 grams of *p*-bromoaniline hydrochloride at 65°, and heated at that temperature for twelve hours. Some nitrogen was evolved during the heating, and the odour of bromobenzene, or possibly of *p*-chlorobromobenzene, was noticed, although neither substance was separated. The resulting mass was treated with concentrated hydrochloric acid, poured into water, collected, washed, and dried. It was then dissolved in toluene, and dry hydrogen chloride was passed through the solution. The precipitate was collected, dried, and treated with ammonia.

The yield was exceedingly small. Subsequent experiments with other acids, such as acetic, benzoic, and sulphuric, gave no better result, and the separation of the base by rendering alkaline with sodium hydrogen carbonate the mass obtained after the twelve hours' heating, and then subjecting it to steam distillation, left a tarry, uncrystallisable residue.

The solid was crystallised from benzene, and after several crystallisations the melting point was constant at 146—147°. It forms red needles, easily soluble in all the organic solvents, and gives a deep orange-red coloration with concentrated sulphuric acid:

0·1384 gave 14·1 c.c. N_2 (moist) at 13° and 730 mm. N = 11·65.
0·1440 „ 0·1530 AgBr. Br = 45·20.
$C_{12}H_9N_3Br_2$ requires N = 11·83; Br = 45·03 per cent.

The *acetyl* derivative was obtained by warming the compound with acetic anhydride and glacial acetic acid. It was crystallised from ethyl acetate, from which it separated in pale yellow needles, melting at 205°:

0·1344 gave 0·1268 AgBr. Br = 40·14.
$C_{14}H_{11}ON_3Br_2$ requires Br = 40·27 per cent.

4 : *4′-Dichloro-2-aminoazobenzene*, $C_6H_4Cl\cdot N_2\cdot C_6H_3Cl\cdot NH_2$.

This was prepared by the same method as that used in the case of the bromo-compound. The yield was exceedingly poor. The product, after being crystallised from benzene, forms bright red plates, with a green reflex, is readily soluble in alcohol, benzene, or petroleum, and gives an orange-red colour to concentrated sulphuric acid, changing to green on dilution. It melts at 140°:

0·0911 gave 12·7 c.c. N_2 (moist) at 22° and 753 mm. N = 15·64.
0·1243 „ 0·1351 AgCl. Cl = 26·87.
$C_{12}H_9N_3Cl_2$ requires N = 15·79; Cl = 26·67 per cent.

The *acetyl* derivative, prepared by warming the azo-compound with acetic anhydride and glacial acetic acid, was crystallised from ethyl acetate. It forms yellow needles, melting at 186°:

0·1136 gave 13·8 c.c. N_2 (moist) at 24° and 756 mm. N = 13·54.
$C_{14}H_{11}ON_3Cl_2$ requires N = 13·64 per cent.

3 : *3′-Dibromodiazoamino*-p-*toluene*,
$CH_3\cdot C_6H_3Br\cdot N_2\cdot NH\cdot C_6H_3Br\cdot CH_3$.

The hydrochloride of the base was obtained by the hydrolysis with concentrated hydrochloric acid of the acetyl derivative, formed by acetylation and subsequent bromination of *p*-toluidine in glacial acetic acid. 9·5 Grams of the base were dissolved in 150 c.c. of water with 8·5 c.c. of concentrated hydrochloric acid; 1·8 grams of sodium nitrite were added to the cooled solution, then excess of sodium acetate. After two hours a yellow solid had separated, which was collected and crystallised from methylated spirit until the melting point was constant at 111°. It forms yellow needles:

0·2856 gave 26·8 c.c. N_2 (moist) at 18° and 760 mm. N = 11·05.

$C_{14}H_{13}N_3Br_2$ requires N = 10·96 per cent.

An attempt was made to transform this substance into the isomeric aminoazo-compound by heating it for some time with one molecular proportion of the hydrochloride of the base and five or six times its weight of the base. No compound could be isolated from the tarry mass extracted by the process described previously.

β-Naphthalenediazoamino-p-*chlorobenzene*, $C_6H_4Cl·N_3H·C_{10}H_7$.

This compound is obtained readily by diazotising β-naphthylamine and adding the solution to *p*-chloroaniline hydrochloride in water, with subsequent addition of sodium acetate. It crystallises from methylated spirit in dark yellow needles, melting at 156°:

0·1110 gave 14·5 c.c. N_2 (moist) at 17° and 756 mm. N = 15·08.
0·1210 „ 0·0611 AgCl. Cl = 12·47.

$C_{16}H_{12}N_3Cl$ requires N = 14·93; Cl = 12·58 per cent.

Action of p-*Chloroaniline and its Hydrochloride on β-Naphthalenediazoamino*-p-*chlorobenzene.*

Five grams of the diazoamino-compound were dissolved in 30 grams of *p*-chloroaniline with 3·1 grams of its hydrochloride at 65°, and heated for twelve hours. On treatment with hydrochloric acid to extract *p*-chloroaniline, a green, tarry solid was left, from which it was found impossible to obtain a crystalline product.

Similar treatment of β-naphthalenediazoamino-*p*-bromobenzene, described by Goldschmidt and Molinari (*Ber.*, 1888, **21**, 2567), with *p*-bromoaniline and its hydrochloride also yielded no definite result.

p-*Chlorobenzeneazo-β-naphthylamine*, $C_6H_4Cl·N_2·C_{10}H_6·NH_2$.

This compound has been described by Meldola and Forster (Trans., 1891, **59**, 690).

The *acetyl* derivative is prepared by heating the azo-compound for twenty minutes on a water-bath with a slight excess of acetic anhydride. It crystallises most readily from ethyl acetate, in somewhat indefinite red crystals, melting at 174°:

0·1191 gave 13·4 c.c. N_2 (moist) at 18° and 748 mm. N = 12·79.

$C_{18}H_{14}ON_3Cl$ requires N = 12·99 per cent.

The *benzoyl* derivative, obtained by the Schotten-Baumann process, crystallises from benzene or glacial acetic acid in red needles, melting at 161°. It is not very soluble in alcohol:

0·1311 gave 12·3 c.c. N_2 (moist) at 19° and 754 mm. N=10·69.
$C_{23}H_{16}ON_3Cl$ requires N=10·89 per cent.

Action of Nitrous Acid on the Azo-compound.—The method adopted was that described by Meldola and East (Trans., 1888, **53**, 465). Three grams of the compound were dissolved in glacial acetic acid at 65° and 0·75 gram (1 mol.) of finely powdered sodium nitrite was slowly added. On keeping, a tarry solid separated, which could not be crystallised; it was therefore boiled for thirty minutes with alcoholic potassium hydroxide, the liquid diluted with water, and the solid collected. On crystallisation from glacial acetic acid, it melted at 158°, and was identified as *p*-chlorobenzeneazo-β-naphthol.

p-*Bromobenzeneazo-β-naphthylamine*, $C_6H_4Br\cdot N_2\cdot C_{10}H_6\cdot NH_2$.

This compound has been described by Meldola and Forster (Trans., 1891, **59**, 690).

The *acetyl* derivative is formed by heating the substance, covered with acetic anhydride, for half an hour on the water-bath. It crystallises from ethyl acetate in fine red needles, melting at 176°:

0·1227 gave 12·3 c.c. N_2 (moist) at 18° and 756 mm. N=11·51.
$C_{18}H_{14}ON_3Br$ requires N=11·43 per cent.

The *benzoyl* derivative, obtained by the Schotten-Baumann process, is readily soluble in glacial acetic acid or benzene, from either of which it is obtained in fine, orange needles, melting at 173°:

0·1397 gave 12·2 c.c. N_2 (moist) at 21° and 758 mm. N=9·91.
$C_{23}H_{16}ON_3Br$ requires N=9·78 per cent.

Action of Nitrous Acid on the Azo-compound.—Meldola and East's method was employed. A solid separated from the acetic acid, which, after three crystallisations from that solvent, melted at 135°, and was identified as *p*-bromobenzeneazo-β-naphthyl acetate (Hewitt and Auld, Trans., 1902, **81**, 1206). Some of it was hydrolysed with boiling alcoholic potassium hydroxide, and the product crystallised from benzene in red needles, melting at 172°. Bamberger (*Ber.*, 1895, **28**, 1222) gives the melting point 172—173° for *p*-bromobenzeneazo-β-naphthol.

p-*Tolueneazo-β-naphthylamine*, $CH_3\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot NH_2$.

This compound has been described by Charrier (*Atti. R. Accad. Sci. Torino*, 1910, **45**, 131). It crystallises from methylated spirit in orange-red needles, melting at 112°.

The *acetyl* derivative is obtained by heating the azo-compound with acetic anhydride for ten minutes on a water-bath. It crystallises readily from methylated spirit in pale orange needles, melting at 142°:

0·1247 gave 15·6 c.c. N_2 (moist) at 20° and 752 mm. N=14·16.
$C_{19}H_{17}ON_3$ requires N=13·86 per cent.

The *benzoyl* derivative, obtained by the Schotten-Baumann process, crystallises from glacial acetic acid or benzene in orange crystals, melting at 163°:

0·1552 gave 16 c.c. N_2 (moist) at 20° and 752 mm. N=11·67.
$C_{24}H_{19}ON_3$ requires N=11·50 per cent.

Action of Nitrous Acid on the Azo-compound.—Using Meldola and East's method, a tarry solid was formed, which could not be crystallised. It was boiled with alcoholic potassium hydroxide, when a solid was obtained which crystallised from benzene in red needles, melting at 135°, and was identified as *p*-tolueneazo-*β*-naphthol.

The Action of p-*Toluidine and its Hydrochloride on β-Naphthalenediazoamino*-p-*toluene.*

The diazoamino-compound was obtained from diazotised *β*-naphthylamine and *p*-toluidine in the usual manner, and purified by crystallisation from benzene.

Ten grams of the pure compound were dissolved in 60 grams of *p*-toluidine with 5·5 grams of its hydrochloride at 60°, and heated for six hours. The product was treated with cold dilute hydrochloric acid, and a brown solid was left, which, after two crystallisations from methylated spirit, melted at 112°, and did not lower the melting point of *p*-tolueneazo-*β*-naphthylamine. Hence it was identified as that compound.

o-*Tolueneazo-β-naphthylamine,* $CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2$.

This compound is produced in the usual manner by adding *o*-toluenediazonium chloride to *β*-naphthylamine hydrochloride in cold aqueous solution, with subsequent addition of sodium acetate solution. It separates as a red solid, and crystallises from methylated spirit in long, dark red needles, melting at 122°. It is readily soluble in benzene or glacial acetic acid, and gives a purple colour with concentrated sulphuric acid:

0·1275 gave 17·9 c.c. N_2 (moist) at 23° and 758 mm. N=15·78.
$C_{17}H_{15}N_3$ requires N=16·09 per cent.

The *acetyl* derivative is formed on heating with acetic anhydride, for twenty minutes on a water-bath. It crystallises readily from ethyl acetate in small, red needles, melting at 150°:

0·1192 gave 14·7 c.c. N_2 (moist) at 20° and 754 mm. N = 14·00.
$C_{19}H_{17}ON_3$ requires N = 13·86 per cent.

The *benzoyl* derivative, obtained by the Schotten-Baumann reaction, crystallises from glacial acetic acid or benzene in orange-red needles, melting at 124°:

0·1050 gave 10·9 c.c. N_2 (moist) at 24° and 758 mm. N = 11·61.
$C_{24}H_{19}ON_3$ requires N = 11·50 per cent.

Action of Nitrous Acid on the Azo-compound.—Using Meldola and East's method, a tarry, uncrystallisable solid was obtained, which was boiled with alcoholic potassium hydroxide for thirty minutes. The solid precipitated by water was crystallised from benzene, when it was obtained in red needles, melting at 130°. It was identified as *o*-tolueneazo-β-naphthol.

Action of β-Naphthalenediazonium Chloride on o-*Toluidine.*

With the intention of obtaining β-naphthalenediazoamino-*o*-toluene, 12 grams of β-naphthylamine were diazotised, and the solution was added to 9 grams of *o*-toluidine in 10 c.c. of hydrochloric acid with 50 c.c. of water. Then excess of sodium acetate solution was immediately added, when a brown solid separated, which, on reaching the ordinary temperature, became oily. It was washed as thoroughly as possible and allowed to remain overnight, when it had solidified to a red solid. On one crystallisation from methylated spirit it melted at 117°, and a second crystallisation raised the melting point to 121°, when it did not affect that of *o*-tolueneazo-β-naphthylamine. It was accordingly identified as this compound.

Reduction of o-*Tolueneazo-β-naphthylamine.*

In order to establish beyond doubt the constitution of the azo-compound obtained in the last experiment as well as that of the specimen obtained from *o*-toluenediazonium chloride and β-naphthylamine, each was treated in the following manner.

Four grams were dissolved in hot glacial acetic acid, and zinc dust was added until the solution was almost colourless. It was diluted, rendered alkaline with sodium hydroxide, and the bases were extracted with ether. After removing the ether, the residue was warmed with acetic acid and acetic anhydride, and after some time the acetyl derivatives were separated by pouring into cold water. The resulting solid mixture was crystallised from alcohol, and separated into two portions, one melting at 234° after recrystallisation, the other at 109°. They were identified as diacetyl-1:2-naphthylenediamine and aceto-*o*-toluidide respectively. This establishes the formula $CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2$ for the azo-compound. Identical results were obtained with the two specimens obtained by the different methods previously mentioned.

m-*Tolueneazo-β-naphthylamine*, $CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2$.

This compound is readily produced by adding *m*-toluenediazonium chloride to β-naphthylamine hydrochloride in cold aqueous solution, with subsequent addition of sodium acetate solution. An orange-red solid separated, and after some time this was collected, washed, and crystallised from methylated spirit. After two crystallisations the melting point was constant at 102°. It forms small, orange-red needles, and gives a deep purple coloration with concentrated sulphuric acid:

0·1561 gave 0·4461 CO_2 and 0·081 H_2O. C = 77·94; H = 5·77.
0·1093 ,, 15·4 c.c. N_2 (moist) at 22° and 754 mm. N = 15·94.
$C_{17}H_{15}N_3$ requires C = 78·16; H = 5·75; N = 16·09 per cent.

The *acetyl* derivative is produced by heating the substance with acetic anhydride on a water-bath for fifteen minutes. It crystallises from ethyl acetate or alcohol in red needles. When the specimen from ethyl acetate is heated quickly it melts at 126°, then appears to resolidify, afterwards melting at 146°. If heated slowly it does not melt at 126°, but some change of colour is apparent, the solid afterwards melting at 146°. When crystallised from alcohol it melted, when heated quickly, at about 140°, but when heated slowly the melting point was 146°. On account of the limited amount of material available, this phenomenon was not studied further, but it may be due to the occurrence of two crystalline modifications:

0·1012 gave 12·6 c.c. N_2 (moist) at 16° and 748 mm. N = 14·05.
$C_{19}H_{17}ON_3$ requires N = 13·86 per cent.

The *benzoyl* derivative obtained by the Schotten-Baumann reaction crystallises from glacial acetic acid in orange needles, melting at 157°:

0·1251 gave 12·9 c.c. N_2 (moist) at 22° and 754 mm. N = 11·59.
$C_{24}H_{19}ON_3$ requires N = 11·50 per cent.

Action of Nitrous Acid on the Azo-compound.—Meldola and East's method gave a tarry, uncrystallisable solid, which was boiled with alcoholic potassium hydroxide. On the addition of water a solid was obtained, which, after three crystallisations from benzene, melted constantly at 137°. It was identified as m-*tolueneazo-β-naphthol*, which seems not to have been described, for it did not lower the melting point of a specimen obtained by the action of *m*-toluenediazonium chloride on alkaline β-naphthol. This specimen also melted at 137°. The azo-compound crystallises in dark red needles:

0·1511 gave 14·4 c.c. N_2 (moist) at 19° and 752 mm. N = 10·83.
$C_{17}H_{14}ON_2$ requires N = 10·68 per cent.

β-Naphthalenediazoamino-m-*toluene*, $CH_3 \cdot C_6H_4 \cdot N_3H \cdot C_{10}H_7$.

Proceeding exactly as described above in the case of *o*-toluidine, the action of β-naphthalenediazonium chloride on *m*-toluidine gave a brown mass, which became tarry on rising to the ordinary temperature, and did not change further on keeping. On the addition of alcohol to the partly dried substance, a tarry compound, which could not be identified, passed into solution, leaving a yellow solid, not readily soluble in alcohol. This was crystallised from light petroleum, from which it separated in slender, yellow plates, melting and decomposing at 183°. On boiling with dilute hydrochloric acid it was decomposed with evolution of nitrogen, and it gave, on analysis, figures agreeing with those required by the diazoamino-compound:

0·0836 gave 11·9 c.c. N_2 (moist) at 18° and 747 mm. N = 16·16.
$C_{17}H_{15}N_3$ requires N = 16·09 per cent.

The yield was very small, and the behaviour of this compound, when heated with *m*-toluidine and its hydrochloride, has not yet been investigated.

Action of β-Naphthol on Diazoamino-compounds.

The method adopted consisted in heating the diazoamino-compound with one molecular proportion of β-naphthol on the water-bath for one hour, and subsequently at 110° for half an hour to complete the reaction. The product was then warmed with dilute hydrochloric acid, collected, and washed. The solid remaining was crystallised from benzene or glacial acetic acid, and identified by its melting point, whilst the filtrate was rendered alkaline with sodium hydroxide, and the amine separated and identified by suitable means.

β-Naphthalenediazoamino-p-*chlorobenzene*.—The amine obtained was identified as *p*-chloroaniline, and no β-naphthylamine could be found. The azo-compound, after two crystallisations from glacial acetic acid, melted at 175°, and did not lower the melting point of β-naphthaleneazo-β-naphthol.

This result agrees with the formula $C_6H_4Cl \cdot NH \cdot N_2 \cdot C_{10}H_7$ for the diazoamino-compound.

β-Naphthalenediazoamino-p-*bromobenzene*.—The amine obtained was identified as *p*-bromoaniline, and no β-naphthylamine could be found. The azo-compound, after three crystallisations from glacial acetic acid, melted at 175°, and did not lower the melting point of β-naphthaleneazo-β-naphthol.

This result agrees with the formula $C_6H_4Br\cdot NH\cdot N_2\cdot C_{10}H_7$ for the diazoamino-compound.

β-Naphthalenediazoamino-p-*toluene*.—The amine obtained melted at 110° before crystallisation, and was pure β-naphthylamine. The azo-compound was crystallised from benzene three times, when it melted at 134°, and did not lower the melting point of *p*-tolueneazo-β-naphthol.

This result agrees with the formula $CH_3\cdot C_6H_4\cdot N_2\cdot NH\cdot C_{10}H_7$ for the diazoamino-compound.

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CCIII.—*The Molecular Condition of Some Organic Ammonium Salts in Bromoform.*

By William Ernest Stephen Turner.

In that section of the author's paper on "Molecular Association and its Relationship to Electrolytic Dissociation" (Trans., 1911, **99**, 880), which deals with the molecular state of organic ammonium salts, the conclusions were drawn that (1) salts of organic ammonium bases are strongly associated in chloroform solution; (2) the degree of association depends on (*a*) the nature of the base, (*b*) the character of the acid, chlorides being least associated, next bromides, and then iodides, when these three classes are compared, (*c*) the concentration of the solution, (*d*) the nature of the solvent, association occurring in solvents of low dielectric constant, electrolytic dissociation in media, like water, of high specific inductive capacity.

The results now presented of the molecular weights of a number of these salts in bromoform appear to the author to provide ample confirmation of his views. The publication of the new data also enables him to refer to certain points in two subsequent publications which have a direct bearing on his work, those, namely, of Hantzsch and Hofmann (*Ber.*, 1911, **44**, 1176) and of Wedekind and Paschke (*Ber.*, 1911, **44**, 3072; 1912, **45**, 1449), in which interpretations of results differ somewhat from his own.

The physical properties of bromoform differ only in degree from those of chloroform, but as its freezing point is slightly below the normal atmospheric temperature only, it possesses not only the advantage of being available for the cryoscopic process, but also, by its use, the investigation of dimethylpyrone hydrochloride, which decomposes on boiling in chloroform, was made possible. On the other hand, as the dielectric constant of bromoform is slightly less than that of chloroform, the solubility of the organic ammonium salts, apart from the lower temperature employed, might be expected to be less (Walden, *Zeitsch. physikal. Chem.*, 1906, **55**, 683; 1908, **61**, 633). So it turned out. To the number of those salts mentioned in the former paper as being too sparingly soluble in bromoform to be of use must be added *n*-propylamine hydrochloride and *iso*amylamine hydrochloride; diethylamine hydrobromide and hydriodide; tetraethylammonium chloride, bromide and iodide, and tetrapropylammonium iodide; and diphenylamine hydrochloride. Twelve salts were found sufficiently soluble, although triethylamine hydriodide but sparingly, and from the dilute solution employed a slight deposition of the salt occurred, so that the result is to be taken rather as an indication of strong association than of quantitative value. It may be mentioned that the solutions in bromoform were coloured slightly brown by the small amounts of tetrapropylammonium iodide and triethylamine hydriodide which entered into solution.

The measurements of molecular weight in bromoform solution indicate that the organic ammonium salts are strongly associated (compare also Wedekind and Paschke, *loc. cit.*). As shown by the table on p. 1926, the monosubstituted ammonium salts are most, the trisubstituted ammonium salts least associated, results in harmony with the behaviour in chloroform. Only one representative of the quaternary ammonium salts could be examined, namely, tetra*iso*amylammonium iodide, and this is strongly associated. Bromides and iodides are, in turn, more strongly associated than chlorides. Dimethylpyrone hydrochloride also shows association in a pronounced degree, and lends support to the author's view that in indifferent solvents all salts would be found associated.

It is in dealing with the effect of concentration on the degree of association that the author's views are not at one with those expressed by Hantzsch and Hofmann and by Wedekind and Paschke. These investigators, in agreement with the author, regard the high molecular weights as due to association and not to polymerisation, and that the association is dependent on the concentration of the solution. Nevertheless, they appear to set inadmissible limits on the degree of association to which a substance can attain. Thus, Hantzsch and Hofmann conclude that the tetraalkylammonium salts behave most simply, since (according to them) their molecular weights are independent of the dilution, and are at most quinquemolecular. Wedekind and Paschke, again, whilst they do not agree that the degree of association of the tetrasubstituted ammonium salts is independent of the concentration, do appear to regard most salts as having an association factor not higher than two. They state also that, from the author's own measurements in chloroform, the salts of fatty-aromatic tertiary bases (for example, of ethyl- and diethyl-aniline) do not possess an association factor essentially greater than two. This is not the author's interpretation, however, nor does it appear to be one that can be made; and the results now recorded with bromoform show its impossibility. The deductions of the investigators referred to have been made, in the author's view, on insufficient data. Neither the constancy of molecular weight of the tetrasubstituted ammonium salts, nor a maximum molecular weight value of either five or two times the normal is borne out by the data, either for solutions in chloroform or in bromoform, as the following selection of values indicates:

Substance.	M.W. (calc.).	Solvent.	Grams salt per 100 grams solvent.	M.W. (obs.)	Association factors.
NEt_4Cl ...	165·6	Chloroform	2·00— 6·43	646— 976	3·90—5·90
NEt_4Br ...	210·1	,,	4·26— 7·97	1410—1794	6·71—8·60
NPr_4I......	313·1	,,	3·21—13·42	1254—1393	4·00—4·45
NAm_4I ...	427·3	Bromoform	0·43— 4·01	667—1463	1·56—3·42

The cryoscopic measurements of Wedekind and Paschke were made only at a single concentration, and the one substance common to their and to the author's investigation, namely, triethylamine hydrochloride, gave an association factor which was distinctly lower than two; but that this figure cannot be taken as the limiting value is obvious from the results now presented, which show that between the concentrations 0·33 and 3·59 per cent., the association factor rises from 1·41 to 2·77 without reaching a limit. The coefficient of increase of molecular weight with concentration, as the author has previously pointed out, differs from salt to salt, and negative values appear to be possible. The coefficient may be so small as to make the molecular weight values apparently stationary. Thus, in chloroform, the molecular weight of ethylaniline hydrochloride only rises from 346 to 353 between the concentrations 2·40 and 4·49 per cent., whilst, in bromoform, the value for methylaniline hydrochloride is practically constant at 366 over the range 1·18 to 4·45 per cent. In neither case is the association factor close to a whole number, however.

Finally, a comparison of the results, at corresponding concentrations, in chloroform and bromoform is interesting. The standard of comparison chosen is that of a dilute solution containing 25 milligram-molecules (calculated on the basis of the formula weight) per 100 c.c. of the solvent, and in the following table the values of the molecular weight and of the association factor (A) at this concentration are given, and of the ratio of A_B for bromoform to A_C for chloroform. The numbers for chloroform have been deduced from the author's ebullioscopic measurements previously given. Triethylamine hydriodide and tribenzylamine hydrochloride are not included, because the solutions available are too dilute for the extrapolation of values, dimethylpyrone hydrochloride because of its instability in chloroform.

Degree of Association at Concentration of 25 milligram-molecules per 100 c.c.

Substance.	M.W. (calc.).	Chloroform.		Bromoform.		
		M.W.	A_C.	M.W.	A_B.	A_B/A_C.
(*iso*)$C_4H_9\cdot NH_2,HCl$......	109·6	498	4·54	469	4·28	0·94
$(C_2H_5)_2NH,HCl$ ...	109·6	277	2·53	332	3·03	1·20
$(C_2H_5)_3N,HCl$	137·6	190	1·38	279	2·28	1·65
$(C_2H_5)_3N,HBr$	182·0	296	1·63	481	2·64	1·62
$(C_3H_7)_2NH,HCl$ ...	137·6	276	2·00	362	2·63	1·31
$(C_5H_{11})_4NI$	427·3	765	1·79	1425	3·33	1·86
$C_6H_5\cdot NH\cdot CH_3,HCl$	143·5	311	2·17	367	2·56	1·18
$C_6H_5\cdot N(C_2H_5)_2,HCl$	185·6	256	1·38	342	1·84	1·33
$C_6H_5\cdot N(C_2H_5)_2,HI$.	277·0	505	1·82	825	2·98	1·58

Apart from *iso*butylamine hydrochloride, the degree of association in bromoform is considerably greater than in chloroform. Two factors may conceivably play a part in producing this increase of association, namely, the lower temperature, and the fact that bromoform has a smaller dielectric constant than chloroform in the ratio 4·51 ($CHBr_3$ at 20·7°) to 5·2 ($CHCl_3$ at 18°) (B. B. Turner, *Zeitsch. physikal. Chem.*, 1900, **35**, 385). As the difference of temperature between the two sets of measurements is but about 54°, and as, from the general experience up to the present, molecular complexity in solution does not appear to vary very much for such a range of temperature, it is almost certain that the lower dielectric constant of bromoform is the main cause of the increased association. The effect of a change of solvent does not appear to be the same for each salt, as indicated by the ratios of the association factors, and there is agreement here with the influence of the solvent on the molecular complexity of amides, anilides, and urethanes (Meldrum and Turner, Trans., 1908, **93**, 876; 1910, **97**, 1605). The author hopes to be able to analyse these results more closely in a subsequent communication.

EXPERIMENTAL.

The salts used in this investigation were purified and treated by the same processes as those employed in the previous research (Trans., 1911, **99**, 880).

To prepare the bromoform for use, it was shaken first with water containing a trace of alkali, then with several quantities of distilled water, dried over fused calcium chloride, and afterwards further purified by freezing out. Distillation under diminished pressure gave a product which, although quite colourless and pure at first, soon began to decompose, so that for purification the process was discarded.

As the only trustworthy density measurements previously made appear to be two values obtained at 15° and at 25° by Perkin (Trans., 1884, **45**, 533), and the density at the freezing point was required in order to deduce the figures given on p. 1926, it was determined on a sample purified by the first method, and D^{7}_{4} found to be 2·9153.

Moisture was excluded from the Beckmann freezing-point apparatus used by the passage through its upper portion of a stream of dry air. The cryoscopic constant of bromoform employed in the calculation of molecular weights is 144.

Molecular-weight Determinations in Bromoform at the Freezing Point.

Diethylamine hydrochloride
(M.W. = 109·6).
Solvent: 26·34 grams.

w.	Δ°.	M.W.	*A.*
0·0614	0·111	300	2·74
0·1505	0·256	321	
0·2532	0·417	333	
0·4666	0·695	367	
0·7000	0·944	405	
0·9260	1·094	463	4·22

Triethylamine hydrochloride
(M.W. = 137·6).
Solvent: 21·84 grams.

0·0716	0·243	194	1·41
0·1744	0·474	243	
0·3590	0·761	311	
0·6220	1·115	368	
0·7844	1·358	381	2·77

Dipropylamine hydrochloride
(M.W. = 137·6).
Solvent: 25·62 grams.

0·1726	0·274	354	2·57
0·4236	0·640	372	
0·6662	1·002	374	
0·8536	1·257	382	2·78

iso*Butylamine hydrochloride*
(M.W. = 109·6).
Solvent: 22·55 grams.

w.	Δ°.	M.W.	*A.*
0·0708	0·104	435	3·97
0·1140	0·161	452	
0·3014	0·401	480	
0·3274	0·449	466	4·25

Triethylamine hydrobromide
(M.W. = 182·0).
Solvent: 24·7 grams.

0·1628	0·289	328	1·75
0·2914	0·391	431	
0·4830	0·522	539	
0·7821	0·669	681	3·74

Triethylamine hydriodide
(M.W. = 229·0).
Solvent: 25·47 grams.

0·0900	0·119	428	1·83

Tetraisoamylammonium iodide
(M.W. = 427·3).

Solvent: 22·24 grams.

w.	Δ°.	M.W.	*A.*
0·0958	0·093	667	1·56
0·2446	0·163	972	
0·4086	0·227	1165	
0·8928	0·395	1463	3·42

Methylaniline hydrochloride
(M.W. = 143·5).

Solvent: 23·68 grams.

0·2786	0·463	366	2·45
0·6124	1·008	369	
1·0536	1·750	366	

Diethylaniline hydriodide
(M.W. = 277·0).

Solvent: 24·40 grams.

0·1692	0·205	487	1·76
0·3774	0·324	687	
0·7644	0·484	932	2·36

Dimethylpyrone hydrochloride
(M.W. = 160·5).

Solvent: 26·10 grams.

w.	Δ°.	M.W.	*A.*
0·0685	0·124	305	1·90
0·1638	0·249	363	

Solvent: 26·04 grams.

0·1260	0·190	357	
0·2512	0·334	416	
0·3078	0·404	421	2·62

Diethylaniline hydrochloride
(M.W. = 185·6).

Solvent: 26·27 grams.

0·1034	0·239	237	1·28
0·2126	0·418	279	
0·5674	0·796	391	
1·0230	1·266	443	2·39

Tribenzylamine hydrochloride
(M.W. = 323·7).

Solvent: 24·99 grams.

0·1268	0·096	373	1·15
0·2134	0·340	362	
0·4156	0·592	404	1·25

The author desires to thank the Government Grant Committee of the Royal Society for a grant which covered the cost of this investigation.

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CCIV.—*The Preparation of Glycogen and Yeast-gum from Yeast.*

By ARTHUR HARDEN and WILLIAM JOHN YOUNG.

SOME time ago (Trans., 1902, **81**, 1224) the authors published a method for the preparation of pure glycogen from yeast. This preparation has since been simplified by adopting the procedure of Pflüger for the preliminary extraction and purification; the preparation may now be carried out in the following manner. The yeast is ground with an equal weight of sand in the machine described by Rowland (*J. Physiol.*, 1901, **27**, 53). It is then extracted by boiling with water, and an equal volume of alcohol added to the cooled and filtered liquid. The precipitate formed is collected, washed with 50 per cent. alcohol, and is then treated on the boiling-water bath with a 60 per cent. solution of potassium hydroxide for two hours. The liquid is cooled and poured into an equal volume of water, filtered, and the filtrate precipitated by the addition of two volumes of alcohol. The precipitate is collected, and washed repeatedly with a mixture containing 400 c.c. of water, 100 c.c. of 50 per cent. potassium hydroxide, and 500 c.c. of alcohol; it is finally washed with 50 per cent. alcohol.

The precipitate is then dissolved in water, and the solution, which is alkaline owing to the difficulty of washing away all the potassium hydroxide, is neutralised with acetic acid, and the glycogen precipitated by the addition of an equal volume of alcohol. By repeatedly dissolving in water, and reprecipitating with alcohol, a preparation may be obtained free from nitrogen and ash, but it still contains the yeast-gum described by Salkowski (*Ber.*, 1904, **27**, 497, 925). This investigator found that yeast-gum is a derivative of mannose; it gives a flocculent precipitate with Fehling's solution, no red coloration with iodine, and, unlike glycogen, is not precipitated by the complete saturation of its solution with ammonium sulphate. The yeast-gum may be removed by redissolving the crude glycogen in water and saturating with ammonium sulphate. The precipitated glycogen, after being washed with saturated ammonium sulphate, is dissolved in water, and the solution again saturated with ammonium sulphate, the process being repeated three times. The final precipitate is again dissolved, the solution dialysed until free from ammonium sulphate, and the glycogen precipitated with alcohol. The last traces of ash are removed by repeatedly dissolving in water and reprecipitating with alcohol. This final purification may conveniently be carried out in a long cylinder, the mixture, after addition of the alcohol, being allowed to stand. The precipitate settles down to the bottom in a few hours, and the liquid may be decanted, the precipitate redissolved in water, and alcohol again added. As the glycogen solution becomes pure and free from electrolytes, the addition of alcohol produces a milky solution instead of a precipitate. This difficulty is easily overcome by the usual method of adding a trace of potassium acetate dissolved in alcohol, which causes the glycogen to precipitate. All traces of the salt are readily removed from the glycogen by washing with 50 per cent. alcohol. Finally, the glycogen is dehydrated with absolute alcohol and ether, and dried in air. When prepared in this way, the glycogen is free from nitrogen, practically free from ash, and contains no yeast-gum, since it gives no precipitate with Fehling's solution. A preparation of glycogen obtained in the above manner contained no nitrogen and 0·02 per cent. of ash.

Yeast-gum may be obtained from the filtrate from saturation with ammonium sulphate by dialysing and precipitating with alcohol. The precipitate is redissolved in a small volume of water, and any trace of glycogen removed by again saturating with ammonium sulphate; the solution is then dialysed, precipitated with alcohol, and the precipitate dehydrated with absolute alcohol and ether. It is obtained in this way as a white powder, dissolving in water to a clear solution, which gives no red colour with iodine, and produces a bulky, flocculent precipitate when warmed with Fehling's solution. A preparation of yeast-gum obtained in this way, after drying in a vacuum at 100°, contained 4·9 per cent. of ash; it was dextrorotatory, having $[\alpha]_D + 66·76°$ (Salkowski gives $+90·1°$ and Loew $+78°$). On hydrolysis, it yielded a reducing sugar; assuming that the sugar exerted a reducing action on Pavy's ammoniacal copper solution equal to that of dextrose, the rotatory power proved to be $[\alpha]_D + 12·8°$ (mannose has $[\alpha]_D + 14·36°$). From the hydrolysis mixture a phenylhydrazone was obtained, which, after recrystallisation, melted at 189—190° (mannosephenylhydrazone melts at 195—200°).

Yeast-juice prepared according to Buchner's method may also serve as a source of glycogen, the juice being boiled, filtered, and precipitated by the addition of alcohol; the precipitate is then treated with potassium hydroxide, and the operations are continued as before.

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CCV.—*The Rate of Reaction of Alkyl Haloids with Certain Tertiary Bases.*

By Richard William Dades Preston and Humphrey Owen Jones.

Part I.

This part of the investigation concerns the velocity-constants for the reaction between methyl, ethyl, propyl, and allyl iodides, the three xylyl bromides, and *p*-bromobenzyl bromide, and the two bases, dimethylaniline and tri*iso*amylamine; the object being to investigate the rate of reaction of the organic haloid, and to ascertain whether the ratio of the rates at which these compounds react is independent of the base.

Determinations of the rate of interaction of bases and halogen compounds have been made by a number of different workers, notably by Menschutkin (*Zeitsch. physikal. Chem.*, 1890, **5**, 589), who measured the velocities of the reaction between aliphatic iodides and triethylamine in a number of organic solvents in order to study the influence of the solvent; by Clarke (Trans., 1910, **97**, 416), who dealt with the action of compounds of the type $X\cdot CH_2\cdot R$ on pyridine, his aim being to study the influence of the nature of the group R on the reactivity of the compound; and by Long (Trans., 1911, **99**, 2164), who measured the velocities of the reaction of alkyl bromides with pyridine and allied cyclic tertiary bases. The latter worker found that *iso*amyl bromide reacts with pyridine, β- and α-picoline, and quinoline about seven times, and *iso*propyl bromide about three times, as rapidly as *iso*butyl bromide. Owing to the general similarity of these bases, great differences in the ratios of the velocity constants are hardly to be expected. It was of interest therefore to ascertain if a large change in the nature of the base produced large changes in the ratios of the velocity constants; and for this reason, the bases dimethylaniline and tri*iso*amylamine, which differ greatly in general chemical characteristics, were selected for the measurements. The solvent used was absolute alcohol, in which the base and haloid were in $N/5$-solution; and the standard temperatures at which the reactions proceeded were 25° and 40°. Owing to the volatility of methyl iodide, the velocity with which this substance acts on the two bases was not measured at 40°, but only at 25°. An approximate value for the velocity-constant at 40° was obtained by multiplying the value at 25° by a factor which expresses the ratio of the velocity at 40° to that at 25°. This factor was obtained by measuring the velocities with which allyl iodide acts on the two bases at 40° and at 25°, and dividing the mean values at 40° by the mean values at 25°. The results are as follow:

$$\text{Dimethylaniline}\frac{\text{velocity of reaction with allyl iodide at }40^\circ}{\text{velocity of reaction with allyl iodide at }25^\circ}=3\cdot31.$$

$$\text{Tri}\textit{iso}\text{amylamine}\frac{\text{velocity of reaction with allyl iodide at }40^\circ}{\text{velocity of reaction with allyl iodide at }25^\circ}=3\cdot43.$$

The values of the velocity-constants and their ratios for eight haloids on the two bases are given in the following tables:

	Dimethyl-aniline, velocity-constant.	Ratio of constants.	Tri*iso*-amylamine, velocity-constant.	Ratio of constants.
Allyl iodide at 40°	$3\cdot57\times10^0$	362·0	$2\cdot25\times10^0$	295
Methyl iodide at 40° (calc.)	$4\cdot73\times10^{-1}$	48·0	$2\cdot50\times10^0$	327
Ethyl iodide at 40°	$3\cdot11\times10^{-2}$	3·2	$3\cdot24\times10^{-2}$	4·2
n-Propyl iodide at 40°......	$9\cdot85\times10^{-3}$	1·0	$7\cdot64\times10^{-3}$	1·0

	Dimethyl-aniline, velocity-constant.	Ratio of constants.	Tri*iso*-amylamine, velocity-constant.	Ratio of constants.
Allyl iodide at 25°	$1{\cdot}08 \times 10^{0}$	—	$6{\cdot}56 \times 10^{-1}$	—
Methyl iodide at 25°	$1{\cdot}43 \times 10^{-1}$	—	$7{\cdot}30 \times 10^{-1}$	—
p-Xylyl bromide at 40° ...	$2{\cdot}32 \times 10^{1}$	3·8	$6{\cdot}8 \times 10^{0}$	4·5
o-Xylyl bromide at 40° ...	$1{\cdot}32 \times 10^{1}$	2·2	$3{\cdot}4 \times 10^{0}$	2·3
m-Xylyl bromide at 40°...	$8{\cdot}62 \times 10^{0}$	1·4	$2{\cdot}7 \times 10^{0}$	1·8
p-Bromobenzyl bromide at 40°	$6{\cdot}03 \times 10^{0}$	1·0	$1{\cdot}5 \times 10^{0}$	1·0

Although the velocity-constants for the four bromides were obtained mainly for another purpose (see part II), they support the conclusions drawn from the results obtained with the iodides.

The most striking feature of the results with the iodides is the interchange of order of reactivity of allyl and methyl iodides on the bases, for, whereas allyl iodide reacts about eight times as fast as methyl iodide on dimethylaniline, it acts slightly less rapidly than methyl iodide on tri*iso*amylamine.

As regards the iodides of allyl, ethyl, and propyl, the ratios of the velocity-constants for dimethylaniline and for tri*iso*amylamine are very similar, the numbers being 362 : 3·2 : 1 and 295 : 4·2 : 1 respectively. The reactivity of these three iodides may be taken therefore as roughly independent of the base. The discordance in the allyl-methyl ratios for the bases (7·6 on dimethylaniline and 0·9 on tri*iso*amylamine) may be due to some anomaly in the behaviour of the methyl iodide, since the allyl-ethyl ratios (362 : 3·2 and 295 : 4·2) and the allyl-propyl ratios (362 : 1 and 295 : 1) for the bases are nearly the same.

This view is confirmed by the results obtained with the three xylyl bromides and *p*-bromobenzyl bromide and the bases dimethylaniline and tri*iso*amylamine. In this set of measurements, not only is the absolute order of reactivity unaltered by a change in the base, but the ratios of the reactivities are almost independent of the base (p-CH_3 : o-CH_3 : m-CH_3 : p-Br = 3·8 : 2·2 : 1·4 : 1 and 4·5 : 2·3 : 1·8 : 1, on dimethylaniline and tri*iso*amylamine respectively).

The facts indicate therefore that the relative reactivities of organic haloids on bases are, in the main, independent of the base.

This conclusion may also be deduced from the ratios of the velocity-constants found by Menschutkin (*loc. cit.*); by Wislicenus (*Annalen*, 1882, **212**, 239), who determined the time required by various alkyl haloids to react completely with ethyl sodioacetoacetate in alcohol; and by Hecht, Conrad and Brückner (*Zeitsch. physikal. Chem.*, 1889, **4**, 273) in their measurements of the rate of ether-formation from alkyl iodides and sodium ethoxide. The results are tabulated below:

Iodide.	Wislicenus.	Menschutkin.	Hecht, Conrad, and Brückner.
Allyl	>157	—	—
Methyl	39	590	36
Ethyl	4·2	5·2	2·8
n-Propyl	1	1	1

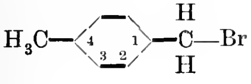
The ratios found in the present investigation agree closely with those above, and the methyl iodide anomaly has its counterpart.

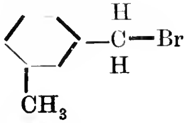
The conclusion may therefore be drawn that the reactivities of organic haloids with bases are conditioned by the specific structure of the alkyl group, and are only influenced in a minor degree by the nature of the substance with which they react.

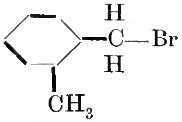
Part II.

An attempt to study the influence of residual valency in an alkyl group on the reactivity of a haloid was also made, in a special instance, by determining the rates at which *o*-, *m*-, and *p*-xylyl bromides and *p*-bromobenzyl bromide act on dimethylaniline. The manner in which considerations of residual valency can be used for the prediction of the order of reactivity of these haloids is readily seen from the following example.

Taking the xylyl bromides first, and considering the effect of the presence of the unsaturated methyl group on the bromomethyl group, in the manner adopted by Flürscheim (Trans., 1909, **95**, 718), it is assumed that the affinity between the carbon atom of the methyl group and the carbon atom of the benzene ring, to which it is attached, is really greater than should be the case normally. The excess of, or residual, affinity will tend to disturb the affinities between the carbon atoms of the ring, and so between them and any groups attached to them. The disturbance produces different effects in each of the three xylyl bromides:


Para.


Meta.


Ortho.

In the case of the para-compound there will be supernormal affinity between the carbon of the methyl group and the carbon atom No. 4 of the benzene ring. The affinity between carbon atoms Nos. 4 and 3 will be decreased, and therefore that between Nos. 3 and 2 increased, in order that there may be no net loss of affinity by No. 3. Between Nos. 2 and 1 the affinity is less than normal, so that between No. 1 and the carbon atom of the CH_2Br-group the affinity is strengthened. The carbon atom of this group will thus be exerting diminished affinity for the bromine atom, so that its reactivity will be a maximum. A thickened line in the formulæ denotes supernormal affinity; a line of the usual thickness denotes subnormal affinity. *p*-Xylyl bromide should therefore react very rapidly. Similar considerations indicate that the reactivity of the meta-compound is a minimum, and that it is again a maximum in the ortho-compound. In the latter compound, the *o*-methyl group would be expected to exert a steric influence tending to lower the reactivity of the CH_2Br-group. The predicted order of reactivity of these compounds would be: para, fastest; ortho, fast; meta, slow.

With regard to *p*-bromobenzyl bromide, the bromine atom is usually considered to be more unsaturated than the methyl group; the disturbance of affinity by the *p*-bromine atom would be greater than that produced by the *p*-methyl group of the *p*-xylyl bromide; the final result being that the affinity between the carbon and bromine atoms of the CH_2Br group is still further lessened, so that *p*-bromobenzyl bromide should be more reactive than *p*-xylyl bromide.

The experimental mean results, with dimethylaniline at 40° in $N/5$-solution in absolute alcohol, are as follows:

	Velocity-constant.		Velocity-constant.
p-Xylyl bromide	$2{\cdot}32 \times 10^1$	*m*-Xylyl bromide..............	$8{\cdot}62 \times 10^0$
o- ,, ,, ...	$1{\cdot}32 \times 10^1$	*p*-Bromobenzyl bromide......	$6{\cdot}03 \times 10^0$

It will be seen that the three xylyl bromides confirm the conclusions deduced above, but the reactivity of *p*-bromobenzyl bromide is less than either of the xylyl bromides, whereas the above view would indicate that it should be greater.

This discrepancy may be due to the greater mass of the bromine atom or to its strongly marked electronegative character. Less accurate measurements of the velocity-constants for the four bromides on tri*iso*amylamine were made, with a view to determining their order of reactivity. Two values of the constant were obtained in each case, and the results show that the order is unchanged:

	Velocity-constant.		Velocity-constant.
p-Xylyl bromide	$6{\cdot}8 \times 10^0$	*m*-Xylyl bromide	$2{\cdot}7 \times 10^0$
o- ,, ,, ...	$3{\cdot}4 \times 10^0$	*p*-Bromobenzyl bromide	$1{\cdot}5 \times 10^0$

EXPERIMENTAL.

I.—*Purification of the Reagents Used.*

(*a*) Dimethylaniline was purified by treatment with acetic anhydride and repeated crystallisation of the sparingly soluble hydrogen oxalate, from which the base was liberated by sodium hydroxide, and redistilled. The pure dimethylaniline boiled at 186°/761 mm.

(*b*) Tri*iso*amylamine was purified by redistillation.

(*c*) The alcohol used as solvent throughout these experiments was purified by treatment with quicklime and then with calcium.

(*d*) The iodides of methyl, ethyl, propyl, and allyl were shaken with very dilute sodium hydroxide solution, and then with distilled water, dried over fused sodium sulphate, filtered from this, and used at once for an experiment. Sometimes, in the case of the iodides of lower boiling point, the iodide was only distilled before use. Compounds purified by either method gave identical results, as may be seen from the identical values of k being obtained in two determinations of the reaction-velocity between allyl iodide and tri*iso*amylamine, for the iodide in one case was distilled, and in the other case was purified according to the first of the above methods.

(*e*) The xylyl bromides and *p*-bromobenzyl bromide had the correct boiling and melting points.

II.—*Procedure.*

The base and the haloid were made up as a $N/5$-solution in the same stock absolute alcohol, at 25°. Equal volumes of the two solutions, usually 100 c.c., but sometimes 150 or 200 c.c. each, were prepared. One solution was then poured into a flask of double its capacity, and then the flasks were left in the thermostat for a short time to acquire the correct temperature. The contents of the smaller flask were then poured into the larger flask, the latter well shaken, and the time of mixing noted. At suitable intervals of time, two volumes of 25 c.c. each of the reacting solution were withdrawn from the flask in the thermostat (in the case of the faster reactions the determinations were not done in duplicate), and poured into two separating funnels of 120 c.c. capacity, each of which contained 25 c.c. of light petroleum and 50 c.c. of $N/20$-nitric acid. The nitric acid at once arrested the reaction by combining with the base, and, on shaking the funnels, the haloid was removed from the aqueous layer by the light petroleum. The lower layer in each case was poured off into a second separating funnel, and the residual alkyl iodide was extracted by a further 25 c.c. of light petroleum. Again, the lower layer was poured off into a small beaker, and the two funnels with the light petroleum were washed out with a small quantity of distilled water. *p*-Bromobenzyl bromide was extracted with ether, and not with light petroleum. In this manner all the alkyl iodide was removed from the quaternary ammonium salt formed in the reaction, for the latter was in the solution of nitric acid and alcohol and water in the beaker. Addition of dilute silver nitrate solution precipitated the iodine of the salt as silver iodide, which was collected and weighed in a Gooch crucible. In all the reactions the silver iodide determinations were done singly, and not in duplicate, after the weight of silver iodide exceeded 0·1 gram.

Although it may be urged that this extraction of the alkyl iodide by light petroleum was unnecessary in the case of propyl iodide, on account of the slowness of its reaction with silver nitrate, yet the extraction was done in this case to keep the results quite comparable, since methyl iodide reacts so quickly with silver nitrate (compare Zeisel's method for the determination of methyl groups) as to render the extraction imperative.

Every iodide was removed in this manner therefore. The loss of salt, as measured by silver iodide, was extremely small.

The same pipette was used throughout the determinations; instead of calibrating it directly, it was thought better to adjust it to deliver such a volume of solution that the solution contained the theoretical amount of ammonium salt, after the extracting process had been performed, as above.

One hundred c.c. of a $N/10$-solution at 25° of phenyldimethylethylammonium iodide three times recrystallised were made in rectified spirit. Twenty-five c.c. of this solution were measured in the pipette, and the ionic iodine in it was estimated as above, after two extractions with light petroleum, etc. The theoretical amount of silver iodide obtainable is 0·5875 gram, and to obtain this the same pipette was always used in a particular way; in four determinations of silver iodide, starting originally with this amount of solution, the weights of silver iodide obtained were 0·5879, 0·5898, 0·5870, and 0·5850 gram respectively.

Throughout all the determinations, therefore, the 25 c.c. pipette was allowed to deliver the main bulk of the solution, and eleven drops more.

It was then necessary to show that the light petroleum extracted all the alkyl iodide and none of the ammonium iodide. One hundred c.c. of rectified spirit solution at 25°, containing 1·315 grams of phenyltrimethylammonium iodide and 1·39 grams of methyl iodide, was made. The ionic iodine in 25 c.c. was estimated as above. In three determinations the weights of silver iodide obtained were 0·2933, 0·2940, and 0·2930 gram respectively. Since the theoretical weight of silver iodide yielded is 0·2938 gram, the conclusion must be drawn that the light petroleum does extract all the methyl iodide and none of the salt, and that the method is set up on a firm experimental basis.

The results are worked out according to the equation for a bimolecular reaction, namely, $k=\frac{1}{t}\cdot\frac{x}{a(a-x)}$, where k is the velocity constant, x is the amount formed, in gram-equivalents of salt per litre, in any interval of time t, and a is the amount of salt that could be formed between the beginning of time t and the completion of the reaction. In the case of the slower reactions, those with ethyl and propyl iodides, the time is reckoned from the time of mixing; but with the faster reactions, the time of the first titration is taken as zero time.

The results obtained in this way are given in the following tables.

Column I contains the time intervals in hours between the titrations; column II contains the weight in grams of silver iodide obtained; column III contains the number of gram-equivalents of the ammonium salt formed, per litre of solution, calculated from the silver iodide weighings; column IV contains the values of the velocity-constant.

*Tri*iso*amylamine.*

Allyl Iodide at 40°.

A.				*B.*			
I.	II.	III.	IV.	I.	II.	III.	IV.
0·0	0·0417	0·0071	—	0·0	0·0395	0·0067	—
0·300	0·0757	0·0129	$2·39 \times 10^{0}$	0·300	0·0736	0·0125	$2·37 \times 10^{0}$
0·667	0·1104	0·0188	2·33	0·667	0·1090	0·0186	2·35
1·15	0·1478	0·0252	2·27	1·15	0·1473	0·0251	2·29
1·72	0·1846	0·0314	2·22	1·75	0·1870	0·0318	2·25
2·35	0·2164	0·0368	2·15	2·52	0·2252	0·0383	2·18
3·05	0·2454	0·0418	2·10	3·52	0·2634	0·0448	2·10
	Mean	......	$2·24 \times 10^{0}$		Mean	....	$2·26 \times 10^{0}$

Allyl Iodide at 25°.

I.	II.	III.	IV.	I.	II.	III.	IV.
0·0	0·0417	0·0071	—	0·0	0·0412	0·0070	—
1·00	0·0747	0·0127	$6·91 \times 10^{-1}$	1·03	0·0750	0·0128	$6·94 \times 10^{-1}$
2·07	0·1049	0·0179	6·84	2·12	0·1050	0·0179	6·73
3·08	0·1286	0·0219	6·62	3·10	0·1282	0·0218	6·56
4·50	0·1566	0·0267	6·40	4·53	0·1584	0·0270	6·50
6·07	0·1847	0·0314	6·28	6·08	0·1851	0 0315	6·33
8·03	0·2156	0·0367	6·27	8·05	0·2160	0·0368	6·30
	Mean	....	$6·55 \times 10^{-1}$		Mean	....	$6·56 \times 10^{-1}$

Methyl Iodide at 25°.

A.				*B.*			
I.	II.	III.	IV.	I.	II.	III.	IV.
0·0	0·0419	0·0071	—	0·0	0·0393	0·0067	—
1·12	0·0808	0·0138	$7·47 \times 10^{-1}$	1·12	0·0783	0·0133	$7·29 \times 10^{-1}$
2·37	0·1182	0·0201	7·39	2·37	0·1160	0·0197	7·32
3·68	0·1508	0·0257	7·32	3·68	0·1493	0·0254	7·30
4·95	0·1790	0·0305	7·32	4·95	0·1767	0·0301	7·25
6·37	0·2060	0·0351	7·30	5·92	0·1951	0·0332	7·18
8·03	0·2313	0·0394	7·15	7·55	0·2226	0·0379	7·13
		Mean	$7·34 \times 10^{-1}$			Mean.........	$7·25 \times 10^{-1}$

Ethyl Iodide at 40°.

0·0	0·0	0·0	—	0·0	0·0	0·0	—
23·0	0·0477	0·0081	$3·83 \times 10^{-2}$	20·2	0·0409	0·0070	$3·72 \times 10^{-2}$
48·0	0·0835	0·0142	3·45	42·9	0·0744	0·0127	3·39
87·5	0·1297	0·0221	3·24	89·7	0·1312	0·0223	3·20
142·0	0·1793	0·0305	3·09	122·0	0·1624	0·0276	3·12
210·0	0·2263	0·0385	2·98	193·0	0·2182	0·0371	3·06
359·0	0·3009	0·0512	2·93	282·0	0·2653	0·0452	2·92
		Mean...... ..	$3·25 \times 10^{-2}$			Mean.........	$3·23 \times 10^{-2}$

n-*Propyl Iodide at* 40°.

A.

I.	II.	III.	IV.
0·0	0·0	0·0	—
47·4	0·0226	0·00385	$8·45 \times 10^{-3}$
145·0	0·0606	0·0103	7·92
285·0	0·1021	0·0174	7·39
363·0	0·1234	0·0210	7·32
451·0	0·1432	0·0243	7·12
		Mean.........	$7·64 \times 10^{-3}$

Dimethylaniline.

(I) *Allyl Iodide at* 25°.

A.				*B.*			
I.	II.	III.	IV.	I.	II.	III.	IV.
0·0	0·0507	0·0086	—	0·0	0·0399	0·0068	—
0·92	0·0927	0·0158	$1·02 \times 10^{0}$	0·90	0·0824	0·0140	$1·00 \times 10^{0}$
1·97	0·1384	0·0236	1·09	2·02	0·1294	0·0220	1·04
3·50	0·1890	0·0322	1·09	3·33	0·1756	0·0299	1·06
6·00	0·2559	0·0435	1·13	6·75	0·2625	0·0447	1·09
8·50	0·3064	0·0522	1·17	8·70	0·3007	0·0512	1·12
		Mean.........	$1·10 \times 10^{0}$			Mean.........	$1·06 \times 10^{0}$

(II) *Allyl Iodide at* 40°.

0·0	0·0421	0·0072	—	0·0	0·0435	0·0074	—
0·250	0·0836	0·0142	$3·52 \times 10^{0}$	0·250	0·0838	0·0143	3·48
0·533	0·1242	0·0211	3·56	0·533	0·1233	0·0210	3·49
0·867	0·1653	0·0281	3·61	0·867	0·1630	0·0277	3·51
1·22	0·2023	0·0344	3·66	1·28	0·2059	0·0351	3·60
1·60	0·2371	0·0404	3·75	1·78	0·2454	0·0418	3·59
		Mean.........	$3·62 \times 10^{0}$			Mean.........	3·53 × 10

(III) *Methyl Iodide at* 25°.

A.

I.	II.	III.	IV.
0·0	0·0229	0·0039	—
4·0	0·0507	0·0086	$1{\cdot}34 \times 10^{-1}$
19·5	0·1397	0·0238	1·39
28·0	0·1780	0·0303	1·41
44·0	0·2370	0·0403	1·44
68·0	0·2954	0·0503	1·43
		Mean.........	$1{\cdot}40 \times 10^{-1}$

B.

I.	II.	III.	IV.
0·0	0·0252	0·0043	—
5·0	0·0616	0·0105	$1{\cdot}45 \times 10^{-}$
20·2	0·1470	0·0250	1·43
28·6	0·1859	0·0316	1·46
44·1	0·2402	0·0409	1·47
53·0	0·2642	0·0450	1·46
68·3	0·3020	0·0514	1·48
		Mean.........	$1{\cdot}46 \times 10^{-1}$

(IV) *Ethyl Iodide at* 40°.

I.	II.	III.	IV.
0·0	0·0296	0·0050	—
22·6	0·0637	0·0108	$3{\cdot}03 \times 10^{-2}$
53·0	0·1032	0·0176	3·04
95·0	0·1544	0·0263	3·20
316·0	0·3056	0·0520	3·26
		Mean.........	$3{\cdot}13 \times 10^{-2}$

I.	II.	III.	IV.
0·0	0·0	0·0	—
17·8	0·0306	0·0052	$3{\cdot}08 \times 10^{-2}$
48·6	0·0776	0·0132	3·13
87·8	0·1253	0·0213	3·08
120·0	0·1582	0·0269	3·07
169·0	0·1999	0·0340	3·05
		Mean	$3{\cdot}08 \times 10^{-2}$

(V) n-*Propyl Iodide at* 40°.

A.

I.	II.	III.	IV.
0·0	0·0351	0·0060	—
125·0	0·0920	0·0157	$9{\cdot}80 \times 10^{-3}$
246·0	0·1384	0·0236	9·96
384·0	0·1778	0·0303	9·66
583·0	0·2285	0·0389	9·83
843·0	0·2801	0·0477	$1{\cdot}00 \times 10^{-2}$
		Mean.........	$9{\cdot}85 \times 10^{-3}$

Dimethylaniline at 40°.

(I) p-*Bromobenzyl Bromide.*

A.

I.	II.	III.	IV.
0·0	0·0692	0·0147	—
0·183	0·1028	0·0219	$5{\cdot}92 \times 10^{0}$
0·367	0·1337	0·0285	6·17
0·567	0·1604	0·0341	6·09
0·800	0·1869	0·0398	6·11
1·07	0·2133	0·0455	6·19
		Mean.........	$6{\cdot}10 \times 10^{0}$

B.

I.	II.	III.	IV.
0·0	0·0674	0·0143	—
0·183	0·1012	0·0215	$5{\cdot}85 \times 10^{0}$
0·458	0·1432	0·0305	5·94
0·667	0·1697	0·0361	5·97
0·900	0·1960	0·0417	6·09
1·17	0·2187	0·0565	6·00
		Mean.........	$5{\cdot}97 \times 10^{0}$

(II) p-*Xylyl Bromide.*

I.	II.	III.	IV.
0·0	0·1350	0·0287	—
0·167	0·2054	0·0437	$2{\cdot}24 \times 10^{1}$
0·333	0·2527	0·0538	2·29
0·500	0·2858	0·0608	2·30
0·667	0·3111	0·0662	2·33
0·833	0·3289	0·0700	2·32
		Mean.........	$2{\cdot}30 \times 10^{1}$

I.	II.	III.	IV.
0·0	0·1631	0·0347	—
0·167	0·2240	0·0477	$2{\cdot}28 \times 10^{1}$
0·343	0·2671	0·0568	2·28
0·500	0·2962	0·0630	2·34
0·667	0·3215	0·0684	2·45
0·833	0·3375	0·0718	2·42
		Mean.........	$2{\cdot}35 \times 10^{1}$

(III) m-*Xylyl Bromide.*

A. I.	II.	III.	IV.	*B.* I.	II.	III.	IV.
0·0	0·0658	0·0140	—	0·0	0·0759	0·0162	—
0·167	0·1131	0·0241	9·26	0·167	0·1206	0·0257	9·14
0·367	0·1560	0·0332	9·11	0·367	0·1600	0·0340	8·77
0·583	0·1891	0·0402	8·74	0·583	0·1917	0·0408	8·51
0·867	0·2232	0·0475	8·56	0·883	0·2258	0·0480	8·26
1·22	0·2513	0·0535	8·10	1·23	0·2520	0·0536	7·82
		Mean.........	8·75 × 10^0			Mean.........	8·50 × 10^0

(IV) o-*Xylyl Bromide.*

0·0	0·0948	0·0202	—	0·0	0·1107	0·0235	—
0·167	0·1511	0·0322	1·33 × 10^1	0·171	0·1638	0·0349	1·34 × 10^1
0·333	0·1922	0·0409	1·32	0·333	0·2017	0·0429	1·33
0·500	0·2251	0·0479	1·33	0·625	0·2489	0·0530	1·31
0·700	0·2575	0·0548	1·37	0·817	0·2709	0·0576	1·29
0·933	0·2774	0·0590	1·27	0·03	0·2903	0·0618	1·27
		Mean.........	1·32 × 10^1			Mean.........	1·31 × 10^1

Triisoamylamine at 40°. (Rough determinations.)

(I.) *p*-Xylyl bromide.				(II.) *o*-Xylyl bromide.			
0·0	0·0	0·0	—	0·0	0·0	0·0	—
0·52	0·1309	0·0279	7·45 × 10^0	0·73	0·1023	0·0218	3·82 × 10^0
1·50	0·2253	0·0480	6·15	1·80	0·1657	0·0353	3·03
		Mean, about......	6·8 × 10^0			Mean, about......	3·4 × 10^0

(III.) *m*-Xylyl bromide.				(IV.) *p*-Bromobenzyl bromide.			
0·0	0·0	0·0	—	0·0	0·0	0·0	—
0·92	0·0985	0·0210	2·90 × 10^0	1·47	0·0826	0·0176	1·45 × 10^0
1·88	0·1504	0·0320	2·51	1·82	0·0976	0·0208	1·45
		Mean, about.........	2·7 × 10^0			Mean, about.........	1·5 × 10^0

Part III.

It might be expected that the reaction-velocity between alkyl haloids and bases could be measured by the change in conductivity of the reaction mixture. The haloid and base in alcoholic solution are non-electrolytes, whilst the ammonium salt formed is an electrolyte. Experiments have shown that the velocity can be measured by the change in conductivity of the solution. The method is a "null" one, in which the conductivity of the reaction mixture is referred to the conductivities of solutions of the salt of known strength.

The procedure is as follows. Equal volumes of *N*/5-solutions of the base and haloid are mixed at the standard temperature, and an electrolytic cell is washed out three times with the solution and then filled with it, the cell and the flask containing the main solution being replaced in the thermostat. At suitable intervals of time the conductivity of the reaction mixture in the cell is taken, and also the amount of iodine in the solution in the flask is estimated, as previously described, the latter process being undertaken to afford values for the velocity-constant which may serve as a check on those obtained by the conductivity method.

The ammonium salt was prepared and purified very carefully, since the successful application of this conductivity method wholly depends on the purity of the ammonium salt. If this is only moderately pure, values for the velocity-constant will be obtained, which, whether they are constant or not, do not agree with those obtained by the direct gravimetric method. The salt, having been obtained pure, is dissolved in known quantities in the same absolute alcohol as was used for the reaction mixture, diluted in various proportions to correspond with the various amounts of salt formed during the reaction, and the conductivities of the solutions are determined. For, since the base and haloid are in $N/5$-solution, the strength of the salt, at 100 per cent. formation, that is, when the reaction is complete, is $N/10$; at 50 per cent. formation, it is $N/20$; at 10 per cent. formation it is $N/100$; and so on. So that made-up solutions of the salt of strengths $N/100$, $N/40$, $N/20$ will represent stages in the reacting mixture at which the salt has been formed to the extent of 10 per cent., 25 per cent., and 50 per cent. In actual practice 50 c.c. of $N/10$-salt in absolute alcohol is made, and this solution is diluted with alcohol, according to the following scheme.

Solutions were made corresponding with 5, 10, 20, 30, 40, and 50 per cent. change.

The conductivity at the standard temperature of each of the six solutions was then determined, three readings being made in each case. From the results a curve was plotted, showing the relation between conductivity and percentage of salt formed, so that, if the conductivity of any solution of this salt is known, the amount of salt corresponding can be at once read from the curve (within the limits of 5 and 50 per cent. formation, that is, between $N/200$ and $N/20$). The amounts of salt which correspond with the conductivities observed when the mixture of base and haloid is in process of reaction can be therefore read from the curve. Accordingly, the amounts of salt formed in the reacting mixture in known intervals of time is determined by utilising the conductivity of the solution instead of by titration. The velocity-constants are then calculated in the usual manner. An objection to the method may at once be raised, for in the reaction mixture there is dimethylaniline and an alkyl haloid, as well as the salt, and the conductivity of this solution is compared with one containing no base or haloid, which is hardly legitimate in view of the probability that the base and haloid would modify the conductivity of the simple salt solution by their viscosity, if for no other reason. The point is an easy one to test, for it so happens that salt solutions, containing the proportions of base or haloid, or both, which would be found at similar concentrations of salt in the reacting mixture, can be made up very simply. Experiment shows that the influence of base and haloid is practically negligible, especially so in the higher concentrations of salt, as may be seen by comparing the results in tables given later.

TABLE I.

Percentage formation of salt.	Percentage of base or haloid remaining.	*N*/10-Salt.	*N*/5-Base.	*N*/5-Haloid.
50	50	mix 10 c.c.	with 5 c.c.	and 5 c.c.
40	60	8 ,,	6 ,,	6 ,,
30	70	6 ,,	7 ,,	7 ,,
20	80	4 ,,	8 ,,	8 ,,
10	90	2 ,,	9 ,,	9 ,,
5	95	1 ,,	9·5 c.c.	9·5 c.c.

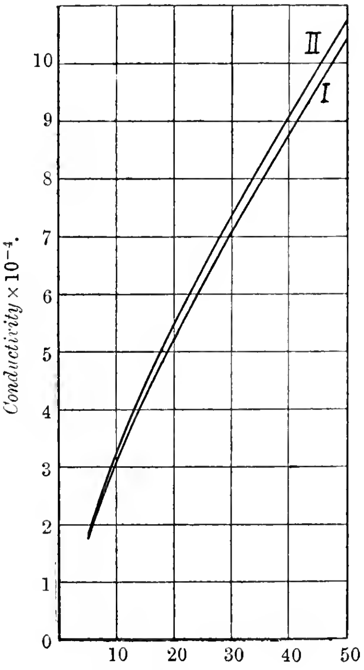
Of course, the base and haloid at once begin to react as soon as they are brought together in the solution, so that this method is only available when the reaction is slow, as in the case of methyl iodide and dimethylaniline, where the increase of conductivity due to the formation of the salt in the short interval of time, about eight minutes, that elapses between the mixing and the conductivity determination, is negligible. In the case of faster reactions, such as those of allyl iodide or the xylyl bromides on dimethylaniline, all that can be done towards determining the effect of free base or haloid on the conductivity of the salt solution is to make up solutions containing the proper proportions of salt and base or haloid, and to compare the conductivities of these solutions with solutions containing the salt only. Appropriate solutions of salt with base or haloid can be made by following table I, and using as the diluent a *N*/10-solution of the base or haloid in absolute alcohol, instead of absolute alcohol.

Preparation of the Salts.

Phenyltrimethylammonium Iodide.—The crude salt was washed with ether, and recrystallised six times from rectified spirit. It melted and sublimed at 218°. (Found, I=48·2. Calc., I=48·3 per cent.)

Phenyldimethylallylammonium Iodide.—This salt was dissolved in acetone, and precipitated by ether seven times. Attempts to grow crystals from acetone solution, as recommended by Harvey (Trans., 1904, **85**, 412), resulted in the reappearance of the oil. The salt was finally obtained in small, colourless grains, melting at 88—89°.

Phenyl-m-*xylyldimethylammonium Bromide*.—A mass of colourless crystals quickly results from mixing molecular proportions of dimethylaniline and *m*-xylyl bromide. On dissolving these in most solvents a deep blue colour appears, and on removal of the solvent, the salt is left as a deep blue oil. After dissolving the oil in acetone, and precipitating with ether several times, the salt is deposited in crystals, with, however, some oil mixed with them. The crystals, originally colourless, soon become pale pink on exposure to air. Light petroleum, however, precipitates the salt from a solution in equal volumes of benzene and acetone in colourless grains. The mass, after the precipitations with ether, is finally purified by two precipitations with light petroleum and one



Percentage formation of salt.

I. *Phenyldimethylallylammonium iodide* (*absolute alcohol*).
II. *Phenyltrimethylammonium* ,, ,, ,,

recrystallisation from acetone, and then the crystalline salt melts at 80°.

I.—*Reaction between Dimethylaniline and Allyl Iodide at 25° in Absolute Alcohol.*

Percentage salt formed.	Volume of *N*/10-salt solution.	Diluent: absolute alcohol, or *N*/10-allyl iodide solution.	Conductivity. I. Alcohol alone.	Conductivity. II. Alcohol + allyl iodide.
50	mix 10 c.c.	with 10 c.c.	$10{\cdot}4 \times 10^{-4}$	$10{\cdot}4 \times 10^{-4}$
40	8 ,,	12 ,,	8·75	8·75
30	6 ,,	14 ,,	7·10	7·08
20	4 ,,	16 ,,	5·25	5·25
10	2 ,,	18 ,,	3·06	3·05
5	1 ,,	19 ,,	1·76	1·79

The first column of conductivity values refers to the conductivities in absolute alcohol: the second column, when *N*/10-allyl iodide solution in absolute alcohol is the diluent. The results show that the influence of the iodide is within the limits of experimental error, except, perhaps, at the highest concentrations of iodide. The effect of dimethylaniline is similarly negligible, as will be shown later from measurements on another salt. Column II in the following table gives the observed conductivities of the reacting mixture at times given in column I; column III gives the corresponding percentage of salt formed in the reacting mixture, the values being obtained from the curve. Column IV gives the values of the velocity-constant, calculated from columns III and I.

Since, hitherto, the velocity-constant has been calculated from gram-equivalents per litre of salt formed, and hours, and since column III gives the salt formed in percentages, the numbers in column III must be divided by 1000 to express the strength in gram-equivalents per litre:

I. Hours.	II. Conductivity.	III. Percentage change.	IV. *k*.
0·0	$2{\cdot}90 \times 10^{-4}$	9·3	—
0·533	3·95	13·7	$1{\cdot}06 \times 10^{0}$
1·68	5·62	22·1	1·08
2·97	7·15	30·3	1·12
4·57	8·48	38·1	1·12
6·38	9·67	45·4	1·14
		Mean	$1{\cdot}10 \times 10^{0}$
		Value directly obtained...	$1{\cdot}08 \times 10^{0}$

II. *Reaction between Dimethylaniline and Methyl Iodide at 25° in Absolute Alcohol.*—The sparing solubility of phenyltrimethylammonium iodide in absolute alcohol necessitated the use of

$N/15$-solutions of salt instead of $N/10$. Owing to the slowness of the reaction, suitable quantities of base and iodide can be brought together into the salt solution.

Percentage formation.	$N/15$-salt.	Absolute alcohol.	Conductivity, alcohol.	$2N/5$-base.	$2N/5$-CH_3I.	Absolute alcohol.	Conductivity in alcohol + methyl iodide and dimethylaniline.
50	15 c.c.	+ 5 c.c.	10·7 × 10^{-4}	2·5 c.c.	+2·5 c.c.	+0·0 c.c.	10·7 × 10^{-4}
40	12 ,,	+ 8 ,,	—	3·0 ,,	+3·0 ,,	+2·0 ,,	9·17
30	9 ,,	+11 ,,	7·43	3·5 ,,	+3·5 ,,	+4·0 ,,	7·32
20	6 ,,	+14 ,,	5·47	4·0 ,,	+4·0 ,,	+6·0 ,,	5·40
10	3 ,,	+17 ,,	3·15	4·5 ,,	+4·5 ,,	+8·0 ,,	3·12
5	1·5 ,,	+18·5 ,,	1·79	4·75 ,,	+4·75 ,,	+9·0 ,,	1·83

The numbers show that the base and haloid have a slight tendency to lower the conductivity.

I. Hours.	II. Conductivity.	III. Percentage change.	IV. k.	AgI in grams.	Salt, gram-equiv. per litre.	k.
0·0	2·27 × 10^{-4}	6·8	—	0·0404	0·0069	—
15·2	5·90	21·9	1·37 × 10^{-1}	0·1298	0·0221	1·38 × 10^{-1}
18·4	6·39	24·4	1·36	—	—	—
24·1	7·27	29·2	1·41	0·1693	0·0288	1·37
39·4	9·10	39·3	1·46	0 2257	0 0384	1·39
42·1	9·42	41·3	1·50	—	—	—
48·1	9·89	44·3	1·50	—	—	—
	Mean		1·43 × 10^{-1}	Mean		1·38 × 10^{-1}

The conductivity method is thus an accurate variant of the direct method of determining reaction-velocities between bases and haloids, but to be successfully applied, it demands extreme purity of all the reagents used.

The expenses of this work were partly defrayed by grants from the Government Grant Committee of the Royal Society, for which the authors are glad to make this acknowledgment.

University Chemical Laboratory,
Cambridge.

CCVI.—*The Action of Sodium Methoxide on 2 : 3 : 4 : 5-Tetrachloropyridine. Part II.*

By William James Sell.

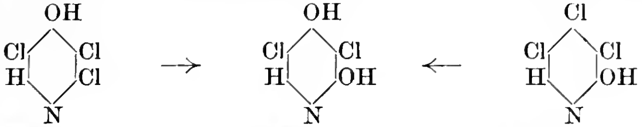
In Part I. (this vol., p. 1193) an account is given of the gaseous products of this reaction when carried out at 200—205° in sealed tubes. The present communication deals (*a*) with the examination of any compounds obtained from the sodium derivatives left in these tubes, and further (*b*) an account is given of the products when the reaction is carried out by heating the mixture in a water-bath in a flask fitted with a reflux condenser, provision being made for the absorption of any methyl ether which may be produced.

(*a*) The only substance obtained from the residue left in the tubes after heating to 200—205° is 3:5-dichloro-2:4-dihydroxypyridine, which forms lustrous needles (m. p. 294°), and the same substance is obtained whether the tubes had been exhausted or not before heating.

(*b*) The reaction in this part of the work was carried out on a fairly large scale, and in two series (*b*1) and (*b*2), the sodium methoxide solution employed differing in concentration and consequently in boiling point. In series (*b*1) the solution of sodium methoxide was only of moderate strength, the products being largely 3:5-dichloro-2:4-dimethoxypyridine (m. p. 57°), with small quantities of 3:5-dichloro-4-hydroxy-2-methoxypyridine (m. p. 174—175°) and 2:3:5-trichloro-4-hydroxypyridine (m. p. 217—218°). No methyl ether was observed in this series. In series (*b*2) the sodium methoxide solution used was of such strength as practically to solidify when cold; a mere trace of 3:5-dichloro-2:4-dimethoxypyridine is obtained, and practically the whole of the tetrachloropyridine is converted into 3:5-dichloro-4-hydroxy-2-methoxypyridine (m. p. 174—175°). Methyl ether was produced in quantity in this series. The production of methyl ether at this low temperature (79—74°), accompanied as it is by the conversion of a methoxy- into a hydroxy-group, confirms the explanation of this occurrence offered in Part I. (*loc. cit.*). With regard to the compounds produced under (*b*1), both 3:5-dichloro-2:4-dimethoxypyridine (m. p. 57°) and 3:5-dichloro-4-hydroxy-2-methoxypyridine (m. p. 174—175°) are converted into 3:5-dichloro-2:4-dihydroxypyridine (m. p. 294°) by hydrolysis at 170° with concentrated hydrochloric acid.

The known readiness with which the halogen in the 2:4-positions is removed by such reagents as sodium methoxide compared with that in the 3:5, renders it extremely probable that the methoxy- and hydroxy-groups concerned in the above-mentioned compounds are in the positions assigned to them. This belief is confirmed by the fact that either of the trichloromonohydroxypyridines having the constitution given below when heated to 180° with sodium methoxide yields the same dichlorodihydroxypyridine (m. p. 294°), identical with the compound obtained by hydrolysis from the above 3:5-dichloro-2:4-dimethoxypyridine and 3:5-dichloro-4-hydroxy-2-methoxypyridine.

In considering the relative positions of the methoxy- and hydroxy-groups in the last-mentioned substance, there is no doubt that the dimethoxy-compound is the chief product in (*b*1)—at or below 70°, the temperature reached in this mixture.



M. p. 218°. M. p. 294°. M. p. 226—227°.

In the series (*b*2) one of the methoxy-groups is shown to have given place to a hydroxy-group at or below the temperature reached by the mixture (79°), the temperature gradually falling as the reaction proceeds, and remaining steady at 74° with the production of 3:5-dichloro-4-hydroxy-2-methoxypyridine and methyl ether, thus:

$$(c)\ \mathrm{RCl} + \mathrm{CH_3{\cdot}ONa} = \mathrm{NaCl} + \mathrm{RO{\cdot}CH_3}.$$

$$(d)\ \mathrm{RO{\cdot}CH_3} + \mathrm{CH_3{\cdot}ONa} = \mathrm{RONa} + (\mathrm{CH_3})_2\mathrm{O}.$$

Noteworthy is the production in small quantity of 2:3:5-trichloro-4-hydroxypyridine in (*b*1) as pointing to the low temperature at which the 4-methoxy-group is attacked by the sodium methoxide, giving the hydroxy-compound melting at 217—218°.

Further, in some experiments in which 3:5-dichloro-4-hydroxy-2-methoxypyridine was heated in sealed tubes with excess of sodium methoxide, there was no alteration at 125° or at 140°, but at 150° the second methoxy-group was attacked, and 3:5-dichloro-2:4-dihydroxypyridine (m. p. 294°) was produced.

EXPERIMENTAL.

(*a*) The residue in the tube was dissolved in water, and treated with a current of steam, when nothing passed over. The residual solution was acidified with sulphuric acid, and the crystalline matter collected and recrystallised from boiling water, in which it is moderately soluble. 3:5-*Dichloro*-2:4-*dihydroxypyridine* forms glistening groups of needles, which are anhydrous, and melt at 294° without decomposition. It is freely soluble in alcohol, and practically insoluble in the usual organic solvents:

0·355 gave 0·56662 AgCl. Cl = 39·46.

$\mathrm{C_5H_3O_2NCl_2}$ requires Cl = 39·44 per cent.

A solution in dilute ammonia after evaporating all excess of ammonia gives the following reactions: (1) With silver nitrate in dilute solution a *silver* compound is gradually deposited in clusters of needles; in more concentrated solution a heavy, white, crystalline precipitate is immediately produced, which is sparingly soluble in boiling water. (2) Mercuric chloride gives no precipitate. (3) Barium chloride produces a white precipitate in spherical groups of needles. (4) The *calcium* compound is soluble.

The apparatus in which both series of experiments (*b*1) and (*b*2) were conducted consisted of a flask with a reflux condenser, to the top of which was fitted a Wöhler tube containing about 20 c.c. of concentrated sulphuric acid to absorb any methyl ether.

(*b*1) To the flask containing about 150 c.c. of dry methyl alcohol in which 9 grams of sodium had been dissolved, were added 20 grams of 2:3:4:5-tetrachloropyridine, and the whole, after cooling in water for a few minutes to restrain the vigour of the reaction, was heated by immersion in a water-bath for six hours. The temperature of the boiling mixture was 70°. The resulting product was distilled in a current of steam, when a considerable quantity of a solid, crystalline substance collected in the receiver. This dissolved freely in hot alcohol, from which it crystallised in colourless, prismatic needles, and on purification melted at 57°. 3:5-*Dichloro*-2:4-*dimethoxypyridine* is freely soluble in alcohol or the usual organic solvents, but is practically insoluble in water:

0·35 gave 0·5125 CO_2 and 0·107 H_2O. C=39·93; H=3·40.
$C_7H_7O_2NCl_2$ requires C=40·38; H=3·36 per cent.

The residue after steam distillation was acidified with sulphuric acid, when a small, crystalline precipitate was obtained. This on purification, by crystallisation from 25 per cent. spirit, was separated into two compounds, one melting at 174—175°, which was recognised as 3:5-dichloro-4-hydroxy-2-methoxypyridine (see below), and the other, melting at 217—218°, as 2:3:5-trichloro-4-hydroxypyridine (Sell and Dootson, Trans., 1903, **83**, 400). (Found, Cl=53·3. Calc., Cl=53·6 per cent.)

In series (*b*1) described above no distinct evidence of methyl ether was obtained. In the experiment (*b*2) 80 c.c. of dry methyl alcohol were used to dissolve 9 grams of sodium, the solution of the latter towards the last being assisted by heating on the water-bath. The rest of the operations were conducted as in (*b*1). There was a trace of the volatile needles of 3:5-dichloro-2:4-dimethoxypyridine in the steam distillate, the only other product beside methyl ether being 3:5-*dichloro*-4-*hydroxy*-2-*methoxypyridine*, which was precipitated from the residual liquid by sulphuric acid, and on purification from much boiling water and also from hot dilute spirit crystallised in colourless needles and plates melting at 174—175°. The substance is freely soluble in alcohol, moderately so in the usual organic solvents or boiling water, and very sparingly so in cold water:

0·163 gave 0·220 CO_2 and 0·038 H_2O. C = 36·8; H = 2·58.
0·327 ,, 0·4742 AgCl. Cl = 36·44.
$C_6H_5O_2NCl_2$ requires C = 37·01; H = 2·57; Cl = 36·59 per cent.

The pure substance distils slowly in a current of steam.

A solution in dilute ammonia after evaporation to remove excess of ammonia gives the following reactions: (1) With silver nitrate a flocculent precipitate sparingly soluble in boiling water, from which it separates on cooling in delicate, microscopic needles. (2) With lead acetate white bunches of needles are slowly deposited. (3) The *barium*, *calcium*, and *magnesium* salts are soluble.

Examination for Methyl Ether.—The sulphuric acid from the Wöhler tube in the experiments from (*b*2) gave a good yield of methyl ether, which was examined in a similar way to that described in Part I. (*loc. cit.*). It was inflammable, and freely soluble in water. The dry gas was liquefiable, and boiled at −21°. A portion exploded with excess of oxygen gave the following results:

Vol. of ether	1·8 c.c.	After KOH	10·4 c.c.
,, ,, + oxygen ...	17·6 ,,	,, pyrogallol	0·0 ,,
After explosion	14·0 ,,	$(CH_3)_2O + 3O_2 = 3H_2O + 2CO_2$	

Conversion of 3:5-*Dichloro*-2:4-*dimethoxypyridine into* 3:5-*Dichloro*-2:4-*dihydroxypyridine.*—Two grams of 3:5-dichloro-2:4-dimethoxypyridine were heated in a sealed tube with 20 c.c. of concentrated hydrochloric acid to 175° for four hours. The product was evaporated to remove excess of acid, and the substance, when crystallised from water, was identified as 3:5-dichloro-2:4-dihydroxypyridine, melting at 294° (uncorr.). (Found, C = 32·96; H = 1·74; Cl = 39·0. Calc., C = 33·33; H = 1·66; Cl = 39·44 per cent.)

Conversion of 3:5-*Dichloro*-4-*hydroxy*-2-*methoxypyridine into* 3:5-*Dichloro*-2:4-*dihydroxypyridine.*—This compound was treated in a similar manner to the preceding one, and gave precisely similar results, the product melting at 294°.

Conversion of 3:4:5-*Trichloro*-2-*hydroxypyridine and* 2:3:5-*Trichloro*-4-*hydroxypyridine respectively into* 3:5-*Dichloro*-2:4-*dihydroxypyridine.*—A specimen of each of these compounds weighing 2 grams was heated in a sealed tube with methyl alcohol, in which 2 grams of sodium had been dissolved, for four hours to 180°. On dissolving the contents of each tube in water, and acidifying the solution, the precipitates obtained from each, after being purified by crystallisation, were found to have identical properties and to melt at 293—294°.

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CCVII.—*Studies in Phototropy and Thermotropy. Part III. Arylideneamines.*

By Alfred Senier, Frederick George Shepheard, and
Rosalind Clarke.

In a previous paper (Senier and Shepheard, Trans., 1909, **95**, 1944) it was suggested that phototropic and thermotropic phenomena should be explained by some less drastic hypothesis than that of intramolecular decomposition and rearrangement, and therefore use was not made of Hantzsch and Werner's hypothesis or of any of its more recent modifications, and, if intramolecular rearrangement is excluded as an explanation, polymorphism is still more so, the same crystal changes backwards and forwards yielding the darker or lighter phototrope or thermotrope at will, without the least indication whatever of change in crystalline form. Moreover, we call attention in this paper to two instances of distinctly dimorphous arylideneamines, in which each of the dimorphic varieties is both phototropic and thermotropic. In one case the two dimorphic varieties exhibit a marked difference in their phototropy. Some new hypothesis is wanted to explain this phenomena, and it seems to us that this may be found in the direction indicated in the paper referred to, that is, by assuming the existence of complex solid molecular aggregates related to gaseous molecules as gaseous molecules are related to atoms.

The Relation of Phototropy to Temperature: A Study of Schiff's Bases or Anils.

Our own experience and that of other workers in phototropy have shown that this phenomenon is influenced to an important degree by temperature; thus Marckwald (*Zeitsch. physikal. Chem.*, 1899, **30**, 140), who first observed phototropy, noticed that in one case, at the ordinary temperature, the effect of exposure to light was rapid, but that the reverse action in the dark was very slow, requiring some twenty-four hours. When, however, the reverse action was tried at a temperature of 90°, the change was instantaneous. Other instances of the influence of temperature on phototropy are mentioned by Biltz (*Zeitsch. physikal. Chem.*, 1899, **30**, 527), and particularly by Stobbe (*Annalen*, 1908, **359**, 1). It seemed to us desirable, first, to study the effect of light, at temperatures up to their melting points, on Schiff's bases, which are known to be phototropic at the ordinary temperature, and secondly, to seek for phototropy among the numerous Schiff's bases, which have not hitherto disclosed that property, at temperatures down to that of solid carbon dioxide.

For the first purpose the following bases, arylideneamines, were selected, all of which are phototropic at the ordinary temperature, and their behaviour was noted, under the influence of light at higher temperatures up to their melting points: Salicylideneaniline, salicylidene-*o*-bromoaniline, salicylidene-*p*-bromoaniline; salicylidene-*m*-toluidine, salicylidene-*o*-4-xylidine, salicylidene-*o*-chloroaniline, salicylidene-*p*-aminobenzoic acid, salicylidene-*o*-anisidine, and disalicylidene-*m*-phenylenediamine. Of these compounds the first three are known, but their phototropic property has not been previously observed; the four following are also known, having been described by us in previous papers, and their phototropy noted; the last two are included among the new compounds described in this paper. Salicylideneaniline was studied by Anselmino (*Ber.*, 1907, **40**, 3473), and by others. It is dimorphous, existing in two distinct crystalline forms (Anselmino). We find that both of these forms are phototropic, and to about an equal degree. Disalicylidene-*m*-phenylenediamine, prepared by us, is an interesting compound. It is also dimorphous; the one form crystallises slowly from light petroleum in long needles, and the other crystallises from alcohol, or, when made to crystallise rapidly from light petroleum, in small plates. These dimorphous varieties are both phototropic, but differ greatly in this respect. The needles are much more sensitive to light than the plates, but the plates revert to the original form more rapidly than the needles.

Salicylideneaniline, salicylidene-*m*-toluidine, salicylidene-*o*-4-xylidine, and salicylidene-*o*-chloroaniline continue to exhibit phototropy to about the same degree up to their melting points. The following bases, however, disclose the fact that there is a limit of temperature below their melting points above which phototropy ceases.

	High temperature limit of phototropy.
Disalicylidene-*m*-phenylenediamine (needles)	75°
Disalicylidene-*m*-phenylenediamine (plates)	30°
Salicylidene-*o*-bromoaniline	65°
Salicylidene-*p*-bromoaniline	48°
Salicylidene-*o*-anisidine	30°
Salicylidene-*p*-aminobenzoic acid	20° (about)

In all cases when the source of light was removed, near the high temperature limit, the reverse change was almost instantaneous.

In order to accomplish our second object, namely, to search for phototropy among Schiff's bases not known to be phototropic, by subjecting them to the action of light at low temperatures, we tried a large number of such bases, condensation products of salicylaldehyde, using ice and salt as a cooling agent. Only one of the bases experimented with showed phototropy, namely, salicylidene-*p*-anisidine, which responded to the influence of light and darkness at −20°. Both salicylidene-*o*-toluidine and salicylidene-*m*-bromoaniline are slightly phototropic at the ordinary temperature, and it was expected that these would show greater activity at lower temperatures. This expectation was, however, not realised; the former was tried at −20°, also with solid carbon dioxide and ether, and the latter at −20°. The possibility that this slight phototropy might be due to a small mixture of phototropic impurity was excluded by careful purification, when the phototropic property persisted unaltered.

No instance has hitherto been observed of phototropy among *o*-hydroxybenzylideneamines in which the benzylidene group is further substituted. We therefore prepared a number of such bases (see below), and examined them for phototropy. None exhibited this property at the ordinary temperature, but one, namely, 2-hydroxy-3-methoxybenzylidene-*p*-xylidine proved to be phototropic at −20°.

The phototropic Schiff's bases vary very greatly in the rapidity with which they undergo the reverse change in the absence of light at the ordinary temperature. The following table shows approximately this relative velocity, under the same conditions, for a few of these bases. The time required by salicylideneaniline is taken as a standard of comparison:

Salicylideneaniline	1
Salicylidene-*o*-chloroaniline	$1\frac{1}{2}$
Salicylidene-*o*-bromoaniline	$1\frac{1}{2}$
Salicylidene-*p*-bromoaniline	$\frac{1}{3}$
Salicylidene-*m*-toluidine	80
Salicylidene-*o*-4-xylidine	3
Salicylidene-*o*-anisidine	$\frac{1}{20}$
Salicylidene-*p*-aminobenzoic acid	4
Disalicylidene-*m*-phenylenediamine (plates)	$\frac{1}{60}$
,, ,, (needles)	9

It is our intention to extend these measurements and to study the effect at different temperatures.

Salicylidene-β-naphthylamine: The Identity of its two Phototropes with the two forms obtained by differences in the method of preparation.

This remarkable arylideneamine, which was originally prepared by Emmerich (*Annalen*, 1887, **241**, 351), was shown in a previous paper (Senier and Shepheard, Trans., 1909, **95**, 1950) to be sensitive to light and heat, giving yellow and red varieties. It has now been found that this compound is phototropic, but that the reverse change at the ordinary temperature is very slow. It is, moreover, one of the class of Schiff's bases which can be prepared at will, in two different forms, also yellow and red. There can be little doubt that these two pairs of yellow and red varieties, the one obtained by variations in the mode of preparation, and the other by phototropic action, are identical. There is no indication of dimorphism, and, unlike the two instances of dimorphic compounds already considered, these preparation varieties do not admit of phototropic modifications, but are themselves identical with phototropic modifications.

When salicylaldehyde is added to an alcoholic solution of β-naphthylamine, the crystals which separate first are always yellow, but they darken when left in contact with the alcohol, in the absence of light, to orange or orange-red. Light being excluded, the shade of colour which results depends on two conditions: first, the concentration of the solution, and secondly, the temperature.

The following table shows the colour of the product obtained when 0·5 gram of β-naphthylamine, dissolved in the quantity stated of 90 per cent. alcohol, was employed, the calculated proportion of salicylaldehyde added, and the separation of the crystals effected at the temperature given. The crystals were kept at the temperature stated until no further change took place, and the colour given is that of the final product. A much longer time is necessary at the lower temperatures to attain this final colour.

	10 c.c.	15 c.c.	20 c.c.	40 c.c.	60 c.c.	80 c.c.	100 c.c.
65°	orange	—	yellow	—	—	—	—
38	orange-red	dark orange	orange	yellow	—	—	—
32	—	—	dark orange	—	—	—	—
28	—	—	orange-red	dark orange	light orange	dark yellow	—
26	—	—	orange-red	—	—	—	—
19	—	—	orange-red	dark orange	orange	—	—
−20	—	—	red	light red	orange-red	orange	light orange

These results show that, in the preparation of this base, the more concentrated the solution employed, or the lower the temperature of the experiment, the redder is the product, whilst the more dilute the solution or the higher the temperature the yellower is the product. When amyl alcohol, instead of ethyl alcohol, is employed, the results are the same, but with acetic acid as a solvent only the yellow form is obtained. If either variety is recrystallised from alcohol, only the yellow modification separates, but this is doubtless due to the sparing solubility of the base in alcohol, which gives a solution too dilute to be capable of yielding the red variety.

The change of red salicylidene-β-naphthylamine, prepared at low temperatures or in concentrated solution, into the yellow variety, identical with the reverse phototropic change, takes place exceedingly slowly at the ordinary temperature; at 40° it requires about fourteen days, but four hours are sufficient at 85°.

Phototropically, yellow salicylidene-β-naphthylamine is readily changed to the red variety at the ordinary temperature when exposed to the light. At the same temperature the reverse change in the dark is very slow, but, as in other cases, the change is more rapid at higher temperatures. Thus, two portions of the red phototrope formed from the yellow by exposure to light were placed in the dark, the one at 48°, which became yellow in fifteen hours, and the other at 32°, which lost most of its red colour in twenty-four hours, but did not lose the last traces of it even after seventy hours. At 110° the yellow form changes to the red when exposed to the light, but quickly returns to the yellow on removal of the illumination. This behaviour is in agreement with the other cases already considered. In all these experiments the comparisons were made at the same temperature in order to exclude thermotropic effects.

The red variety is not acted on by light, although a difference is noticed between the exposed and the unexposed substance at the ordinary temperature; this, however, is due to the unexposed substance becoming paler in colour owing to some conversion into the yellow form. If the red salicylidene-β-naphthylamine is kept at a temperature of −20° in order to stop the change to yellow of the unexposed substance, no difference in colour can be detected between this product and that exposed to light at the same temperature.

It was hoped that further material for the study of colour changes, like those exhibited by Emmerich's base, might be afforded by its analogues in which substitution had taken place in the salicylidene groups. With this view we prepared a series of such derivatives (described below), but in no case was there any indication of a second coloured variety, or of phototropy.

It appears therefore that the red base, prepared under special conditions, agrees exactly with the new phototrope obtained from the yellow base by the action of light: first, in not being further changed by light, and secondly, in its changing into the yellow variety at a certain velocity at certain temperatures. There can therefore be little doubt that the red and yellow bases prepared under special conditions are identical with the red and yellow bases obtained from the former bases by phototropy; thus, in the case of salicylidene-β-naphthylamine, each of its two phototropes can be prepared without phototropic action by taking advantage of other suitable conditions. This base is therefore distinctly unlike the bases, salicylideneaniline and disalicylidene-*m*-phenylenediamine, where their two dimorphous forms are not related as phototropes to each other, but are, as already pointed out, themselves phototropic.

New Schiff's Bases, Arylideneamines, prepared in the course of this inquiry.

In nearly all cases these bases were prepared by adding an alcoholic solution of the aldehyde to a calculated proportion of the amine dissolved in the same solvent, and the resulting product was recrystallised from light petroleum. All the bases described dissolve readily in the usual organic solvents.

*Salicylidene-*o*-anisidine*, $OH\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot OMe$, crystallises in deep yellow prisms, melting at 58° (corr.). It is phototropic at the ordinary temperature and at temperatures up to 30°, and the change from the dark to the light phototrope is very rapid:

0·2546 gave 14·0 c.c. N_2 (moist) at 19° and 764 mm. N=6·36.
$C_{14}H_{13}O_2N$ requires N=6·17 per cent.

*Salicylidene-*m*-anisidine* separates from alcohol in deep yellow needles, melting at 60° (corr.). It is not phototropic:

0·2236 gave 12·4 c.c. N_2 (moist) at 18° and 759 mm. N=6·39.
$C_{14}H_{13}O_2N$ requires N=6·17 per cent.

*Salicylidene-*m*-bromoaniline*, $OH\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4Br$, crystallises from alcohol in deep yellow prisms, melting at 96—97° (corr.). It is very slightly phototropic at the ordinary temperature; exposure to light, however, at −20° did not increase the phototropy:

0·2335 gave 10·7 c.c. N_2 (moist) at 17° and 755 mm. N=5·28.
$C_{13}H_{10}ONBr$ requires N=5·08 per cent.

*Disalicylidene-*o*-phenylenediamine*, $C_6H_4(N{:}CH\cdot C_6H_4\cdot OH)_2$, separates from alcoholic solution in orange needles, which were purified by dissolving in hot benzene and then adding an equal volume of hot light petroleum. It melts at 166° (corr.), and is not phototropic:

0·2136 gave 16·9 c.c. N_2 (moist) at 18° and 747 mm. N=8·98.
$C_{20}H_{16}O_2N_2$ requires N=8·86 per cent.

Disalicylidene-m-*phenylenediamine* exhibits dimorphism. On crystallisation from alcohol, it separates in small plates; from light petroleum, however, if the solution is allowed to crystallise slowly, it separates in long needles, but if crystallisation is made to proceed rapidly, plates similar to those which separate from alcohol are obtained. Both forms exhibit phototropy, but not to the same extent. With the same exposure, the plates do not become as dark as the needles, and return to the lighter coloured modification much quicker. The plates are not phototropic above 30°, whilst the needles exhibit this property up to 75°. Both forms, on prolonged exposure to light, show a further darkening in colour, which does not disappear on keeping in the dark, and is no doubt due to decomposition in the molecule. The substance melts at 109—110° (corr.):

0·1943 gave 15·1 c.c. N_2 (moist) at 18° and 763 mm. N=9·01.
$C_{20}H_{16}O_2N_2$ requires N=8·86 per cent.

2-*Hydroxy*-m-*tolylidene*-β-*naphthylamine*,
$OH\cdot C_6H_3Me\cdot CH{:}N\cdot C_{10}H_7$,
crystallises in pale yellow needles, melting at 94° (corr.). It is not phototropic even at −20°:

0·1217 gave 0·3690 CO_2 and 0·0617 H_2O. C=82·69; H=5·67.
$C_{18}H_{15}ON$ requires C=82·70; H=5·80 per cent.

6-*Hydroxy*-m-*tolylidene*-β-*naphthylamine* separates in microscopic, orange crystals, melting at 160—161° (corr.). No phototropy was observed, although experiments were tried at −20°:

0·1112 gave 0·3367 CO_2 and 0·0577 H_2O. C=82·55; H=5·81.
$C_{18}H_{15}ON$ requires C=82·70; H=5·80 per cent.

5-*Bromosalicylidene*-β-*naphthylamine*, $OH\cdot C_6H_3Br\cdot CH{:}N\cdot C_{10}H_7$, forms pale yellow crystals, melting at 158—159° (corr.). It is not phototropic at the ordinary temperature or at −20°:

0·1078 gave 0·2463 CO_2 and 0·0367 H_2O. C=62·31; H=3·81.
$C_{17}H_{12}ONBr$ requires C=62·55; H=3·71 per cent.

2-*Hydroxy*-3-*methoxybenzylideneaniline*,
$OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_5$,
forms orange prisms, melting at 83° (corr.):

0·1634 gave 9·0 c.c. N_2 (moist) at 19° and 764 mm. N=6·38.
$C_{14}H_{13}O_2N$ requires N=6·17 per cent.

2-*Hydroxy*-3-*methoxybenzylidene*-o-*toluidine*,
$OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_4Me$,
crystallises in fibrous, orange needles, melting at 62° (corr.):

0·1702 gave 8·7 c.c. N_2 (moist) at 18° and 755 mm. N=5·86.
$C_{15}H_{15}O_2N$ requires N=5·81 per cent.

2-Hydroxy-3-methoxybenzylidene-p-*toluidine* forms bright orange needles, melting at 100° (corr.):

0·2018 gave 10·4 c.c. N_2 (moist) at 19° and 757 mm. N = 5·77.
$C_{15}H_{15}O_2N$ requires N = 5·81 per cent.

2-Hydroxy-3-methoxybenzylidene-m-4-*xylidine*,

$OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_3Me_2$,

separates in bright orange needles, melting at 103° (corr.):

0·1671 gave 8·0 c.c. N_2 (moist) at 19° and 760 mm. N = 5·50.
$C_{16}H_{17}O_2N$ requires N = 5·49 per cent.

2-Hydroxy-3-methoxybenzylidene-p-*xylidine* crystallises in deep yellow prisms, melting at 105° (corr.). It is phototropic at −20°, but not at the ordinary temperature:

0·1911 gave 9·4 c.c. N_2 (moist) at 19° and 759 mm. N = 5·64.
$C_{16}H_{17}O_2N$ requires N = 5·49 per cent.

2-Hydroxy-3-methoxybenzylidene-o-4-*xylidine* forms deep orange prisms, melting at 59—60° (corr.):

0·1654 gave 8·1 c.c. N_2 (moist) at 20° and 758 mm. N = 5·59.
$C_{16}H_{17}O_2N$ requires N = 5·49 per cent.

2-Hydroxy-3-methoxybenzylidene-o-*chloroaniline*,

$OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_4Cl$,

crystallises in orange needles, melting at 123° (corr.):

0·1996 gave 10·1 c.c. N_2 (moist) at 19° and 758 mm. N = 5·80.
$C_{14}H_{12}O_2NCl$ requires N = 5·71 per cent.

2-Hydroxy-3-methoxybenzylidene-m-*chloroaniline* separates in deep orange prisms, melting at 79° (corr.):

0·1740 gave 8·8 c.c. N_2 (moist) at 18° and 759 mm. N = 5·83.
$C_{14}H_{12}O_2NCl$ requires N = 5·71 per cent.

2-Hydroxy-3-methoxybenzylidene-p-*chloroaniline* crystallises in bright orange needles, melting at 111° (corr.):

0·2080 gave 10·6 c.c. N_2 (moist) at 19° and 760 mm. N = 5·86.
$C_{14}H_{12}O_2NCl$ requires N = 5·71 per cent.

2-Hydroxy-3-methoxybenzylidene-o-*bromoaniline*,

$OH\cdot C_6H_3(OMe)\cdot CH{:}N\cdot C_6H_4Br$,

forms orange needles, melting at 115—116° (corr.):

0·2144 gave 8·6 c.c. N_2 (moist) at 19° and 769 mm. N = 4·67.
$C_{14}H_{12}O_2NBr$ requires N = 4·58 per cent.

2-Hydroxy-3-methoxybenzylidene-m-*bromoaniline* crystallises in deep orange prisms, melting at 101·5° (corr.):

0·1674 gave 6·8 c.c. N_2 (moist) at 20° and 767 mm. N = 4·69.
$C_{14}H_{12}O_2NBr$ requires N = 4·58 per cent.

*2-Hydroxy-3-methoxybenzylidene-*p*-bromoaniline* separates in deep orange needles, melting at 117° (corr.):

0·1633 gave 6·7 c.c. N_2 (moist) at 21° and 768 mm. N=4·73.
$C_{14}H_{12}O_2NBr$ requires N=4·58 per cent.

*2-Hydroxy-3-methoxybenzylidene-*o*-anisidine*,
$OH\cdot C_6H_3(OMe)\cdot CH:N\cdot C_6H_4\cdot OMe$,
forms deep orange needles, melting at 88—89° (corr.):

0·1590 gave 7·8 c.c. N_2 (moist) at 20° and 767 mm. N=5·65.
$C_{15}H_{15}O_3N$ requires N=5·45 per cent.

*2-Hydroxy-3-methoxybenzylidene-*m*-anisidine* crystallises in orange needles, melting at 80—81° (corr.):

0·1951 gave 9·2 c.c. N_2 (moist) at 19° and 767 mm. N=5·47.
$C_{15}H_{15}O_3N$ requires N=5·45 per cent.

*2-Hydroxy-3-methoxybenzylidene-*p*-anisidine* forms orange needles, melting at 95° (corr.):

0·1566 gave 7·4 c.c. N_2 (moist) at 19° and 766 mm. N=5·48.
$C_{15}H_{15}O_3N$ requires N=5·45 per cent.

2-Hydroxy-3-methoxybenzylidene-β-naphthylamine,
$OH\cdot C_6H_3(OMe)\cdot CH:N\cdot C_{10}H_7$,
crystallises in orange-red needles, melting at 101° (corr.). It is not phototropic at the ordinary temperature or at −20°:

0·1069 gave 0·3054 CO_2 and 0·0534 H_2O. C=77·91; H=5·58.
$C_{18}H_{15}O_2N$ requires C=77·93; H=5·46 per cent.

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CCVIII.—*Properties of Mixtures of Allyl Alcohol, Water, and Benzene. Part II.*

By THOMAS ARTHUR WALLACE and WILLIAM RINGROSE GELSTON ATKINS.

IN the previous part of this paper (this vol., p. 1179) it was shown that allyl alcohol and water form a mixture boiling constantly at 88°, and containing 72 per cent. of the former component.

The present paper deals with the mixture of allyl alcohol and benzene mentioned by Rylands (*Amer. Chem. J.*, 1899, **22**, 384), and also with the ternary mixture, allyl alcohol, water, and benzene.

To obtain these mixtures the components were distilled together in varying proportions, and the fractions of constant boiling point collected. To determine their compositions the three methods employed in the case of the binary * mixture of alcohol and water were used, namely, the bromine-absorption titration and density-composition diagram in the case of the alcohol, Young's middle-point distillation method for all three components, and in addition direct measurement of the volume in the case of benzene after complete extraction of the alcohol by washing repeatedly with water.

It was thus found that the binary mixture of alcohol and benzene contained 17·36 per cent. of the former component. It boils constantly at 76·75°. The corresponding values obtained by Young and Fortey (Trans., 1903, **83**, 45; 1902, **81**, 717) with *n*-propyl alcohol are 16·9 per cent. and 77·1°. Rylands (*loc. cit.*) gives the amount of allyl alcohol as 20 per cent., the mixture boiling at 76·5°. However, as the alcohol he employed boiled at 95·5° and the benzene at 79·2°, as against 96·93° and 80·12°, we have used our own values in subsequent calculations.

The mixture of the three components of constant boiling point was in like maner ascertained to have the following percentage composition: alcohol, 9·16; benzene, 82·26; water, 8·58. It boils at 68·21°, corrected for emergent column error and to normal pressure, as are all the boiling points recorded throughout this paper. These figures may be compared with the corresponding percentages for the ternary mixture with *n*-propyl alcohol boiling at 68·5°, as given by Young and Fortey (*loc. cit.*), namely, alcohol, 9·00; benzene, 82·40; and water, 8·60 per cent.

The great similarity between the alcohol-benzene, alcohol-water (allyl alcohol 72·00 per cent., b. p. 88·0°; propyl alcohol 71·69 per cent., b. p. 87·7°), and alcohol-benzene-water mixtures in the case of allyl and propyl alcohols is noteworthy, seeing that these two substances are chemically so unlike. Physically, however, they are very similar. The agreements noted above are far closer than those between *n*- and *iso*-propyl alcohols, or, indeed, between any other pair of alcohols the data for which are known. It seems that such behaviour is due to the presence of unbranched chains containing the same number of carbon atoms, as distinguished from branched and unbranched chains of equal carbon content.

EXPERIMENTAL.

Kahlbaum's allyl alcohol, employed throughout this investigation, was distilled through a five-section Young evaporator still-head, and a fraction boiling at 97·04—97·08° and having D_{0}^{0} 0·86911 was collected for use. These values probably denote a slightly purer product than that recorded in our previous paper, namely, b. p.

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* The binary and ternary mixtures referred to throughout are the respective mixtures of constant boiling point.

96·93—96·95° and D_0^0 0·86929. The benzene employed was freed from thiophen, fractionated, and the portion which passed over at 80·12—80·16° was collected.

The Distillation of Allyl Alcohol and Benzene.

The mixtures recorded in table I were distilled through a five-section Young evaporator still-head, and the first fraction of each was collected up to the middle point between the boiling points of the binary mixture and the component in excess. The composition of the binary mixture was then calculated by the middle-point method (S. Young, "Fractional Distillation," Ch. xvi.). Redistillation of these first fractions furnished a mixture of constant boiling point, which was collected and analysed.

TABLE I.

	Alcohol in excess.		Benzene in excess.	
	I.	II.	III.	IV.
Weight of alcohol taken ...	53·00	34·39	22·73	14·91
,, benzene ,, ...	53·00	48·35	146·77	98·70
Per cent. of alcohol in binary mixture, by middle-point method	15·94	15·35	17·27	17·39
B. p. of binary mixture	76·77°	76·75°	76·73°	76·78°

Analysis of Redistilled Binary Mixture, b. p. 76·73°.

	Bromine method.	Density curve.	Volume method.
Alcohol..	17·36 *	17·86	17·80

* Mean of three independent determinations, which gave 17·22, 17·47, and 17·38 per cent. respectively.

It is clear that when alcohol is in excess, the results obtained for this component by the middle-point method are too low, whereas when benzene is in excess the agreement between the values afforded by this and the bromine-absorption method is very close. Great accuracy cannot be expected by interpolation on the density-composition curve in this instance, as the compositions of the two mixtures employed were of necessity so close together in order to avoid possible curvature, and as the difference in density between the pure components was not very great. The densities were determined as described in part I.

Table of Densities and Expansions.

I. Alcohol, per cent.	II. D_0^0 found.	III. D_4^0 found.	IV. D_4^0 calculated.	V. Vol. of a gram found.	VI. Vol. of a gram calculated.	VII. Expansion, per cent.
0·00	0·90018	0·90006	0·90006	1·1110	1·1110	0·000
15·81	0·89344	0·89332	0·89504	1·1194	1·1173	0·188
18·77	0·89240	0·89228	0·89404	1·1207	1·1184	0·205
100·00	0·86911	0·86900	0·86900	1·1507	1·1507	0·000

Direct reading of the volume of the well-washed benzene seems to be quite a satisfactory method of analysis, although hardly so accurate as direct reading with the same meniscus in both cases, namely, in titration after adding bromine. Accordingly, it seems best to take the composition of the binary mixture from the last-mentioned method, which is very close indeed to the mean of the determinations made by distillation with benzene in excess.

The Distillation of Allyl Alcohol, Water, and Benzene.

Ternary mixtures of composition, as given in table II, were distilled through the still-head before employed, and the fractions up to and between the several middle points were collected and weighed.

TABLE II.

B. p. of binary mixtures, alcohol–water 88·00°, alcohol–benzene 76·73°, benzene–water 69·25°.

	I.	II.	III.	IV.	
	Residual liquid.				
	Alcohol–benzene binary mixture.	Alcohol.	Water.	Benzene.	
Weight of alcohol taken ...	17·34	48·74	45·08	30·04	
,, benzene ,, ...	82·52	103·66	86·12	212·52	
,, water ,, ...	4·91	2·16	49·77	2·61	
Total	104·77	154·56	180·97	245·17	
Per cent. composition of ternary mixture by middle-point method :					Mean.
Alcohol	—	10·95	8·77	9·32	9·68
Benzene	—	78·89	85·19	81·64	81·90
Water..........	9·14	10·16	6·04	9·04	8·59
B. p. of ternary mixture......	68·18°	68·20°	68·18°	68·12°	

Analysis of the Ternary Mixture.

The combined fractions up to the first middle point were redistilled, and as soon as the boiling point became constant at 68·21°, several small fractions were collected and analysed in their entirety, some for allyl alcohol, and the remainder for benzene. This procedure is necessary in order to ensure that the samples have the composition of the ternary mixture, since the latter consists of two phases.

The estimations of the alcohol by titration and of the benzene by direct reading of the volume are given below:

	Alcohol in mixture, per cent.		Benzene in mixture, per cent.
	9·014		82·21
	9·162		82·18
	9·307		82·38
Mean	9·161	Mean	82·26

On comparing the above figures with the means of those afforded by the middle-point method, it will be seen that the agreement is very close in the case of water, although less so for allyl alcohol, the benzene occupying an intermediate position.

Considering the results of the individual middle-point experiments, it is clear that those yielded by the fourth mixture are in much closer agreement with those arrived at by direct analysis than are the other three sets. This may be partly due to the larger volume of the mixture taken, but it should be noted that in this case benzene was the residual liquid. That the agreement should be closer under these conditions is quite in accordance with the results of distillation of the alcohol-benzene mixtures, where, as before remarked, the best results are obtained when the latter component is in excess. The mixture containing both benzene and water in excess has to be avoided on account of the binary mixture given by these components boiling at 69·25°, which is only one degree above the boiling point of the ternary mixture.

Mixture of Allyl and n-*Propyl Alcohols.*

In the course of the work we redistilled some commercial "allyl alcohol puriss," and obtained nearly 300 grams boiling at 97·03—97·06°, this, lying between the values furnished by two other samples, 96·93—96·95°, D_0^0 0·86929, and 97·04—97·08°, D_0^0 0·96911, we believed to be pure. The value, however, obtained for its density, namely, D_0^0 0·84750, showed that it contained an impurity of lower density. Analysis by the bromine-absorption method gave the values 57·28 and 57·50, mean 57·39, for the percentage of allyl alcohol present. *n*-Propyl alcohol boils at 97·20°, and has D_0^0 0·81936 (Fortey and Young, Trans., 1902, **81**, 717), so it seemed probable that this was the impurity present, especially as allyl alcohol yields *n*-propyl alcohol when heated with potassium hydroxide (Tollens, *Annalen*, 1873, **159**, 92). Assuming *n*-propyl alcohol to be the impurity, the following calculations were made.

Density and Contraction.

D^0_0 found.	D^0_0 calculated.	D^0_4 found.	D^0_4 calculated.	Vol. of a gram found.	Vol. of a gram calculated.	Contraction, per cent.
0·84750	0·84731	0·84739	0·84720	1·1803	1·1831	0·237

To find the percentage composition of the mixture, taking w_1 to be propyl alcohol, D^0_0 0·81936:

$$\frac{100}{0{\cdot}84750}=\frac{w_1}{0{\cdot}81936}+\frac{100-w_1}{0{\cdot}86911},$$

whence $w_2=58{\cdot}05$, correcting for the contraction by substituting D^0_0 (calc.) 0·84731 for D^0_0 found in the above formula, gives 57·67 per cent. allyl alcohol, which is sufficiently close to 57·39, the value found by bromine-absorption, to leave but little doubt that *n*-propyl alcohol was the other component of the mixture.

The compositions and boiling points of the binary mixtures of propyl alcohol with water and with benzene (Young and Fortey, *loc. cit.*) are so close to the figures given above for the corresponding mixtures with allyl alcohol that separation by distillation is impracticable. Fractional crystallisation after cooling in liquid air was no more successful. Such a mixture was, of course, useless for this research.

Conclusion.

Pure allyl alcohol has D^0_0 0·86911, and boils at 97·06°. It forms the following mixtures of constant boiling point.

Alcohol, per cent.	Benzene, per cent.	Water, per cent.	Boiling point.
72·00	—	28·00	88·00°
17·36	82·64	—	76·75
9·16	82·26	8·58	68·21

The alcohol when mixed with water shows a large, and with *n*-propyl alcohol a slight, contraction in volume; with benzene, however, there is a small expansion.

The above data show that if the aqueous solution of allyl alcohol, obtained in its preparation by the usual method, is distilled, the products are the binary mixture of alcohol and water and either alcohol or water. By addition of benzene in the proper proportions and further distillation, it is possible to obtain about 55 per cent. of the alcohol content of the binary mixture in a pure and anhydrous condition. The alcohol in the ternary and binary mixtures collected in this distillation may then be extracted with water, and from the extract the binary mixture of alcohol and water may be removed by distillation and the treatment with benzene repeated.

We wish to express our thanks to Prof. Sydney Young for the use of apparatus, and for placing his experience at our disposal throughout this research. We are also indebted to the Research Fund Committee of the Chemical Society for a grant, which has in part defrayed the expenses of this investigation.

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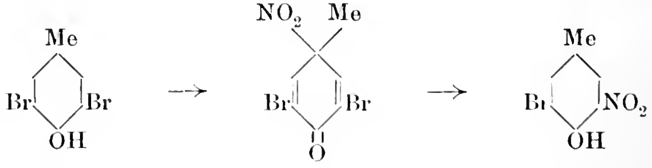
CCIX.—*The Migration of the* para-*Halogen Atom in Phenols.*

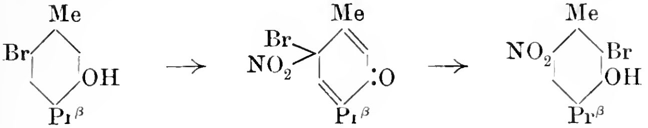
By Philip Wilfred Robertson and Henry Vincent Aird Briscoe.

It has frequently been observed, even under the mildest conditions of nitration, that the nitro-group is capable of displacing a bromine atom in a phenol; thus W. Robertson (Trans., 1902, **81**, 1475) showed that nitric acid converted 2:6-dibromo-4-acetylaminophenol in dilute acetic acid solution into the *o*-nitro-derivative with liberation of bromine. Again, Dahmer (*Annalen*, 1904, **333**, 346) has shown that nitrous acid is capable of changing dibromothymol into bromonitrothymol. In these and similar cases it is extremely probable that the phenol reacts in the tautomeric hemiquinonoid form, as is indicated by an observation of Auwers (*Ber.*, 1902, **35**, 457) that in the action of nitrogen peroxide on a benzene solution of dibromo-*p*-cresol (I) the unstable intermediate compound (II), the formation of which is demanded by such an assumption, could actually be isolated:



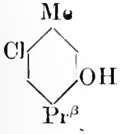
(I.) (II.) (III.)

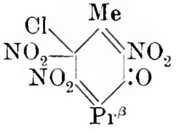
The observation that a nitro-group can displace a para-halogen atom and cause it to migrate into the ortho-position, as was shown in the case of 6-bromothymol (IV) when nitrated in dilute acetic acid solution (P. W. Robertson, Trans., 1908, **93**, 793), appears to be an isolated one. It would seem in this case also that an intermediate compound (V) might be formed:

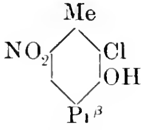

(IV.) (V.) (VI.)

In the hope of throwing greater light on this somewhat peculiar transformation, this reaction has been further studied, and the investigation has been extended to other phenolic derivatives.

When 6-bromothymol was acted on by nitrogen peroxide in chloroform solution at −20° in the expectation of isolating the above intermediate compound (V), the chief product of the reaction was found to be 6-nitrothymol. 6-Chlorothymol (VII), however, when treated under the same conditions with nitrogen peroxide, yielded, not the intermediate compound, but its dinitro-derivative (IX):


(VII.)


(IX.)


(VIII.)

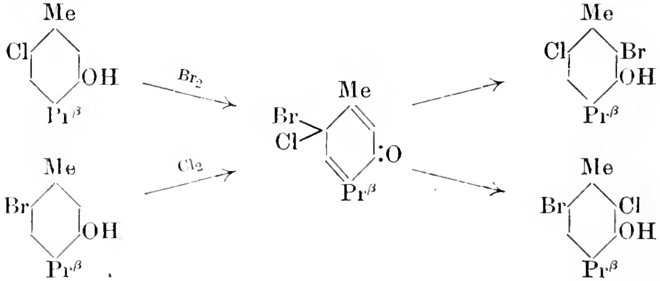
6-Chlorothymol also differed in its behaviour from the corresponding 6-bromo-derivative in that on nitration in dilute acetic acid solution it formed, in addition to 2-chloro-6-nitrothymol (VIII), considerable quantities of 6-nitrothymol and 2:6-dinitrothymol. When, however, the nitration was performed by the action of dilute aqueous nitrous acid on chlorothymol dissolved in light petroleum, or by shaking an ethereal solution with 25 per cent. nitric acid, the action took place more smoothly, and 2-chloro-6-nitrothymol was obtained. In passing, both these methods of nitration may be recommended when the ordinary means of nitrating by nitric acid in dilute acetic acid solution tends to give a mixture of products.

When 6-iodothymol was nitrated in acetic acid solution, iodine was immediately liberated, and a mixture of nitrothymols appeared to be formed. It seems that the heavier iodine atom cannot migrate with sufficient velocity into the 2-position, or that it is unable to enter owing to steric hindrance, and is consequently set free as elementary iodine.

Similarly, experiments with 5-chlorocarvacrol and the corresponding bromo-compound showed that ordinary nitration produced a mixture of dinitro- and 5-nitro-3-halogen derivatives, although here the milder methods of nitration failed to yield a pure product.

It has frequently been suggested that phenols react also in chlorination and bromination in the tautomeric hemiquinonoid form. The production of the para-derivative, often without the slightest trace of ortho, in so many cases of bromination is explained easily in the light of such a theory, and the immense difference in the rates of bromination, visible easily to the eye, of a phenol itself and its para-bromo-derivative is yet another indication; in fact, the immense velocity of bromination, of the same order of magnitude as an ionic reaction, observed by Bruner (*Zeitsch. physikal. Chem.*, 1902, **41**, 513) appears to be compatible only with the assumption of a migrating hydrogen atom.

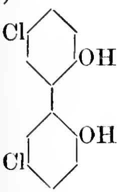
This being so, it seemed natural to expect that 6-chlorothymol on bromination and 6-bromothymol on chlorination would yield the same intermediate hemiquinonoid derivative; and that, as both halogens would have a tendency of the same order to migrate, in comparison with a halogen and a nitro-group, there would be produced a mixture of isomeric chlorobromothymols. This has actually been found to be the case, so that these changes might be formulated as follows:



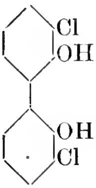
As the products of these two reactions were oils, recourse was had to an indirect method of investigation. It has been shown by Kehrmann (*Annalen*, 1900, **310**, 89) that 2:6-dibromothymol and 2:6-dichlorothymol both give on oxidation with chromic acid in dilute acetic acid solution a quantitative yield of the corresponding thymoquinone. In our experiments there was obtained a mixture of quinones, which, after steam distillation, was dissolved in ether and the ethereal solution washed with aqueous potassium hydroxide to remove any trace of unaltered chlorobromothymol. The proportions of the two halogens in the product were then determined, and it was found that of the chlorine present in 6-chlorothymol 46 per cent. had migrated into the 2-position on bromination; and of the bromine present in 6-bromothymol 17 per cent. had migrated on chlorination.

From this it is evident that the chlorine atom displays a greater tendency to migrate than the bromine atom, as might be expected from its smaller mass.

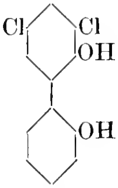
2:2′-Diphenol, the derivatives of which owing to their comparatively high melting points tend less to separate as oils, was found to be a convenient substance for this investigation. On chlorination it yielded a mixture of two dichloro-derivatives, melting at 170° and 129° respectively, and both these isomerides gave the same dichlorodinitro-2:2′-diphenol on nitration. It is assumed that the former is the 5:5′- (I), and that the latter is the 3:3′-compound (II):



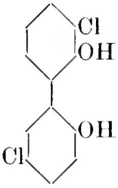
(I.)



(II.)



(III.)



(IV.)

That the two halogen atoms are not in the same nucleus is evident, because in this case (III) it would be impossible to obtain the same dinitro-derivative from both isomerides without a migration of a chlorine atom from one nucleus to the other, an assumption which is extremely improbable. On the assumption that only the ortho- and para-hydrogen atoms (with respect to the hydroxy-group) have been replaced, as is always observed on the mild chlorination of phenols, the only other possibility is that one of the compounds possesses the 3:5′-configuration (IV). To explain the production of the same substance on nitration in this instance it would be necessary to assume that one of the chlorine atoms had migrated. At all events these compounds furnish another example of the migration of halogen on nitration, and, from analogy to the behaviour of the thymol and carvacrol derivatives, it is probable that the para-chlorine atoms have migrated in the formation of this dichlorodinitro-2:2′-diphenol.

Attempts to prove that the nitro-groups occupied the para-position were made by reduction to the amino-compound and subsequent oxidation, in the hope of obtaining dichloro-2:2′-diquinone. The product of this reaction, however, was so insoluble in all solvents that it could not be conveniently investigated.

On attempting to prepare dichlorodinitro-2:2′-diphenol by the chlorination of 5:5′-dinitro-2:2′-diphenol, it was found that a mixture of products was obtained. Strangely enough, chlorine had no action on 3:3′-dinitro-2:2′-diphenol in acetic acid solution, even at 100°.

The two isomeric dichloro-2:2′-diphenols appear to yield a mixture of products on bromination, but in both cases the same dichlorodibromo-2:2′-diphenol (m. p. 185°) could be isolated, so that it is evident that halogen migration has occurred here as in the bromination of 6-chlorothymol.

5:5′-Dibromo-2:2′-diphenol on nitration and 5:5′-dinitro-2:2′-diphenol on bromination yielded the same dibromodinitro-2:2′-diphenol, so that, as in the case of the thymol and carvacol derivatives, the para-bromine atoms have migrated on nitration. 3:3′-Dinitro-2:2′-diphenol was not attacked by bromine as by chlorine.

Experimental.

6-*Chlorothymol.*

This compound has been obtained previously by the action of thionyl chloride on thymol (Bocchi, *Gazzetta*, 1896, **26**, ii, 403; Peratoner, *ibid.*, 1898, **28**, i, 214), but a more convenient method of preparation has been found in the direct chlorination of thymol (30 grams) in acetic acid solution with chlorine evolved from potassium permanganate (12·6 grams) and excess of dilute hydrochloric acid. The product is precipitated with water, the oil separated and dissolved in light petroleum (b. p. 60—80°), and the solution washed repeatedly with water to remove acetic acid, which tends to make the product separate as an oil. Finally, the solution is dried, evaporated to small bulk, and cooled in a freezing mixture of ice and crystallised calcium chloride, when a considerable proportion of the 6-chlorothymol separates in fine crystals, the yield of the pure substance being about 50 per cent. of the theoretical.

6-Chlorothymol prepared in this way is a colourless, crystalline substance, melting sharply at 58°, even after repeated crystallisation from light petroleum, so that the melting points previously given as 58—60° (Bocchi, *loc. cit.*) and 62—64° (Peratoner, *loc. cit.*) must be considered as incorrect. That it has the chlorine in the 6-position is shown by the fact that on oxidation with chromium trioxide it yields thymoquinone.

Nitration of 6-*Chlorothymol.*

Twenty-five grams of 6-chlorothymol were dissolved in glacial acetic acid and treated with 85 c.c. of a 10 per cent. solution of nitric acid in the same solvent, care being taken to keep the temperature below 20°. Excess of water was added, and the precipitated oil was dissolved in light petroleum, from which crystals gradually separated. On recrystallisation from a mixture of benzene and petroleum the substance melted sharply at 140°, the melting point of 6-nitrothymol, and when it was mixed with this substance the melting point remained unchanged.

After evaporation of the petroleum an oily residue was left which could not be crystallised. In order to investigate its nature, it was reduced with tin and hydrochloric acid in alcoholic solution, oxidised with excess of ferric chloride, and the product distilled in a current of steam. An orange-coloured, crystalline substance was obtained, which, after systematic fractionation from benzene and light petroleum, was found to consist of three separate compounds:

(*a*) An orange substance melting indefinitely in the neighbourhood of 118°, which, in spite of repeated attempts to obtain it pure by fractional crystallisation and fractional sublimation, gave on analysis values for chlorine always somewhat too low for chlorohydroxythymoquinone, $C_{10}H_{11}O_3Cl$. It had all the properties of an hydroxyquinone, dissolving completely in aqueous alkali to form a purple solution, and is most probably 2-chloro-5-hydroxythymoquinone mixed with a small quantity of hydroxythymoquinone (*b*).

(*b*) A yellow substance melting at 165°, identical with a preparation of 2-hydroxythymoquinone obtained by the reduction and oxidation of dinitrothymol (compare Mazzara, *Ber.*, 1890, **23**, 1390).

(*c*) A red, somewhat insoluble substance, melting at 224°, which contained no halogen, and gave on analysis numbers agreeing with those required for dihydroxythymoquinone, $C_{10}H_{12}O_4$. This substance has been described by Ladenburg and Engelbrecht (*Ber.*, 1877, **10**, 1218) as melting at 220°, and was obtained by the hydrolysis of 5-chloro-2-hydroxythymoquinone.

The formation of these various compounds indicates that, in addition to 6-nitrothymol, 2:6-dinitrothymol and 2-chloro-6-nitrothymol must have been produced in the nitration of 6-chlorothymol.

When, however, the nitration is performed with nitrous acid, pure 2-chloro-6-nitrothymol is obtained. Two grams of 6-chlorothymol were dissolved in light petroleum, and this solution was floated on a considerable volume of water containing 2 grams (3 mols.) of sodium nitrite and excess of hydrochloric acid, and allowed to remain. After a week the light petroleum had evaporated, and a crystalline product was left. This melted at 112°, after one recrystallisation from alcohol at 116°, the melting point of 2-chloro-6-nitrothymol, and was identified as this substance by the mixed melting-point method.

Similarly, a 10 per cent. ethereal solution of 6-chlorothymol left in a stoppered bottle with 25 per cent. aqueous nitric acid for a week gradually became yellow, and, on evaporation of the ether, there was left a film of crystals of 2-chloro-6-nitrothymol.

With a view to isolating, if possible, the intermediate compound believed to be formed in the nitration of 6-chlorothymol, 6 grams of that substance were dissolved in about 50 c.c. of dry chloroform, cooled to −20° in a freezing mixture, and treated with excess of dry nitrogen peroxide gas prepared by heating dry lead nitrate. The solution, originaly colourless, became yellow, and on addition of a considerable volume of light petroleum (b. p. 40—60°) a pale yellow, crystalline compound separated. This was collected and dried, and then melted with violent decomposition at about 105°. Attempts were made to recrystallise it from alcohol and from chloroform, but in each case it decomposed, giving an oily product. The original substance, however, appeared to be pure, and it was therefore dried over sulphuric acid under diminished pressure for half-an-hour and analysed. The results agreed with those required by 6-*chloro*-2:5:6-*trinitro*-1-*methyl*-4-iso*propyl*cyclo*hexadiene*-3-*one* (IX):

0·1055 gave 0·0460 AgCl. Cl = 10·8.

0·2279 „ 26·8 c.c. N_2 at 21° and 759·4 mm. N = 13·6.

$C_{10}H_{10}O_7N_3Cl$ requires Cl = 11·1; N = 13·2 per cent.

Nitration of 6-*Bromothymol.*

It has already been shown that 6-bromothymol, on nitration by the usual methods, gives 2-bromo-6-nitrothymol. When 5 grams of pure 6-bromothymol were treated in chloroform solution with excess of nitrogen peroxide at −20°, the product, when precipitated by light petroleum, was found to melt sharply at 140°, and was identified with 6-nitrothymol by the mixed melting-point method.

Nitration of 6-*Iodothymol.*

On slowly adding a 10 per cent. solution of nitric acid in glacial acetic acid to 5 grams of 6-iodothymol dissolved in 100 c.c. of acetic acid, the liquid turned brown immediately, and before all the nitric acid had been added crystals of iodine separated.

Nitration of 5-Chlorocarvacrol.

The nitration was performed in the usual manner in cold acetic acid solution, and the product, which was found to be an uncrystallisable oil, was reduced with tin and hydrochloric acid in dilute alcoholic solution, and then oxidised with ferric chloride and distilled in a current of steam, as in the case of the product from the nitration of 6-chlorothymol. A mixture of crystalline hydroxyquinones was obtained, from which were isolated by fractional crystallisation:

(*a*) 5-Chloro-2-hydroxythymoquinone (m. p. 121°), which appears to be the same compound as that (m. p. 122°) obtained by Ladenburg and Engelbrecht (*loc. cit.*) by the reduction and subsequent oxidation of the chloride of 2:6-dinitrothymol.

(*b*) 2-Hydroxythymoquinone, melting at 170°; the same substance as that obtained by Mazzara (*loc. cit.*) by the reduction and oxidation of 3:5-dinitrocarvacrol.

(*c*) Dihydroxythymoquinone (see above), produced by the hydrolysis of the chlorohydroxythymoquinone.

These results indicate that the products of the nitration of 5-chlorocarvacrol are 5-nitro-3-chlorocarvacrol and 3:5-dinitrocarvacrol. The method of nitration with nitrous acid was tried in this case also, but proved unsuccessful.

Bromination of 6-Chlorothymol.

Five grams of pure 6-chlorothymol were dissolved in glacial acetic acid, cooled, and treated with 4·9 grams of bromine (1 mol.) in acetic acid solution. Water was added, the precipitated oil was dissolved in ether, and the ethereal solution washed repeatedly with water. The ether was evaporated off, and the uncrystallisable residue was dissolved in glacial acetic acid and treated with successive small portions of a solution of sodium dichromate in the least possible amount of warm water, until 2·5 grams of the salt (a slight excess over the calculated amount) had been added. During the reaction the solution was cooled in ice, and when all the dichromate had been added it was allowed to remain for half-an-hour in order to make certain that the oxidation was complete. The product was precipitated with water, separated, and distilled in a current of steam; all the substance passed over within a short time, and collected as an oil under the aqueous distillate. This oil could not be made to solidify, and was, presumably, a mixture of quinones; it was purified from any trace of chlorobromothymol by dissolving it in ether, and washing the solution three times with dilute aqueous sodium hydroxide. This solution was finally dried and freed from ether by evaporation.

To ascertain the relative proportions of chloro- and bromo-thymoquinones in the product, about 0·3 gram was oxidised with nitric acid in the presence of excess of silver nitrate in a sealed tube at 200° in the usual manner. The mixed silver haloids thus obtained were dried and transferred to a weighed porcelain boat, which was then heated, first in air to ensure that there was no loss in weight, and afterwards in a stream of chlorine to a temperature just below the fusing point of the silver salts until the weight was constant. It was thus found that 0·1766 gram of the mixed silver chloride and bromide gave 0·1551 gram of silver chloride, whence it may be calculated that of the total halogen in the mixed quinones 44 per cent. was bromine and 56 per cent. was chlorine. Therefore, on bromination of 6-chlorothymol, a considerable proportion of the chlorine must have wandered into the 2-position in the molecule.

Chlorination of 6-*Bromothymol.*

In view of the result of the foregoing experiment it seemed of interest to ascertain in a similar way the result of chlorinating 6-bromothymol. Five grams of pure 6-bromothymol were dissolved in acetic acid, and treated with chlorine (1 mol.) evolved from 1·4 grams of potassium permanganate and excess of dilute hydrochloric acid. The product was precipitated with water, extracted with ether, and oxidised with sodium dichromate in acetic acid solution as described above, and the mixed quinones were freed from any trace of unaltered chlorobromothymol by shaking the ethereal solution repeatedly with alkali. A small quantity of the mixture was then converted into silver haloids, and these were treated with chlorine as before.

It was found that 0·1837 gram of the mixed silver haloids gave 0·1746 gram of silver chloride, from which it follows that of the total halogen in the mixed quinones 17 per cent. was bromine and 83 per cent. was chlorine; thus, in this case also, there is a migration of the 6-halogen atom—the bromine—to the 2-position.

5 : 5′-*Dichloro*-2 : 2′-*diphenol.*

This compound was prepared by passing chlorine, evolved from potassium permanganate (21 grams) and excess of hydrochloric acid, into a solution of 2 : 2′-diphenol (31 grams) in glacial acetic acid. On addition of water the product was precipitated as a solid, which was collected and dried. By crystallisation from hot benzene it was sharply separated into two fractions, the less soluble of which melted at 166—168°, and after recrystallisation at 170°:

0·2414 gave 0·2702 AgCl. Cl=27·8.

$C_{12}H_8O_2Cl_2$ requires Cl=27·8 per cent.

3 : 3′-*Dichloro*-2 : 2′-*diphenol*.

The more soluble fraction of the product of the chlorination of diphenol was precipitated from benzene solution by addition of light petroleum. The crude substance softened at 110°, and did not melt until about 140°; this was probably due to the presence of a small quantity of tetrachlorodiphenol, as was indicated by the high percentage of chlorine found on analysis (29·2 per cent., instead of 27·8 per cent.). By systematic fractionation from benzene and light petroleum a substance was obtained, which melted somewhat indefinitely at 129°, but was undoubtedly 3 : 3′-*dichloro*-2 : 2′-*diphenol*:

0·3120 gave 0·3504 AgCl. Cl=27·8.

$C_{12}H_8O_2Cl_2$ requires Cl=27·8 per cent.

3 : 3′-*Dichloro*-5 : 5′-*dinitro*-2 : 2′-*diphenol*.

This compound was produced when 3 : 3′-dichloro-2 : 2′-diphenol (5 grams) was nitrated with the calculated amount (2·5 grams, 2 mols.) of nitric acid in 10 per cent. acetic acid solution.

After repeated crystallisation from mixtures of acetic acid and water the substance melted sharply at 180°.

5 : 5′-Dichloro-2 : 2′-diphenol, when similarly treated, gave a substance which, after recrystallisation, also melted sharply at 180°. A mixture of the two materials melted at 180°, and this was unchanged on re-melting after solidification. The product of nitration of both 3 : 3′- and 5 : 5′-dichloro-2 : 2′-diphenol is therefore the same substance, namely, 3 : 3′-*dichloro*-5 : 5′-*dinitro*-2 : 2′-*diphenol*:

0·1268 gave 0·1049 AgCl. Cl=20·4.

$C_{12}H_6O_6N_2Cl_2$ requires Cl=20·6 per cent.

Dichlorodibromo-2 : 2′-*diphenol* and *Dichlorobromo*-2 : 2′-*diphenol*.

When 3 : 3′-dichloro-2 : 2′-diphenol was brominated in acetic acid solution, the product melted, after recrystallisation from benzene and alcohol, at 185°; from the bromination of 5:5′-dichloro-2:2′-diphenol was obtained on two occasions a substance melting also at 185°, and identical with the above, as was proved by the mixed melting-point method. This substance is *dichlorodibromo-2:2′-diphenol*:

0·1872 gave 0·3007 AgCl + AgBr. Cl + Br = 56·0.

$C_{12}H_6O_2Cl_2Br_2$ requires Cl + Br = 55·9 per cent.

In one experiment, however, the product of the reaction seemed less pure, and from it was eventually isolated a substance melting at 190°, giving on analysis numbers corresponding with *dichlorobromo-2:2′-diphenol*:

0·1088 gave 0·1528 AgCl + AgBr. Cl + Br = 44·7.

$C_{12}H_7O_2Cl_2Br$ requires Cl + Br = 45·3 per cent.

Attempts to prepare dichlorodibromo-2:2′-diphenol by the chlorination of 5:5′-dibromo-2:2′-diphenol were unsuccessful, the chlorine being absorbed very slowly, with the production of a complex mixture of substances.

3:3′-*Dibromo*-5:5′-*dinitro*-2:2′-*diphenol*.

This compound was obtained when 5:5′-dibromo-2:2′-diphenol was nitrated with nitric acid (2 mols.) in acetic acid solution, or when 5:5′-dinitro-2:2′-diphenol was treated with bromine (2 mols.) under similar conditions. The product in either case was precipitated with water, and, after recrystallisation from alcohol, melted at 201°. A mixture of the products from the two methods of preparation melted at 200°, and even after resolidification the melting point remained unchanged:

0·2118 gave 0·1860 AgBr. Br = 37·3.

$C_{12}H_6O_6N_2Br_2$ requires Br = 36·9 per cent.

Attempts to prepare 3:3′-dibromo-2:2′-diphenol by the action of bromine on the 5:5′-disulphonic acid and subsequent elimination of the sulphonic acid groups were unsuccessful, tetrabromo-2:2′-diphenol being the chief product of the bromination, so that it was impossible to obtain the dibromodinitro-derivative from this substance. On treating 3:3′-dinitro-2:2′-diphenol in acetic acid solution with bromine there was no reaction even at 100°.

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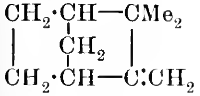
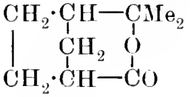
CCX.—*The Constitution of Camphene. Part I. The Structure of Camphenic Acid.*

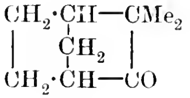
By Walter Norman Haworth and Albert Theodore King.

A survey of the work of recent years bearing on the constitution of camphene will serve to convince one of the considerable body of evidence existing in favour of the acceptance of Wagner's formula (I).

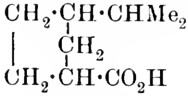
With ozone, camphene forms an ozonide which, on decomposition, gives rise to formaldehyde, camphenilone, and dimethylnorcampholide; and by direct synthesis the constitution of the last-named product has been established by Komppa and Hintikka (*Ber.*, 1909, **42**, 898) as represented by formula (II); consequently the structure of camphenilone is probably represented by (III) (Harries and Palmén, *Ber.*, 1910, **43**, 1432; Semmler, *Ber.*, 1909, **42**, 246):


(I.)


(II.)


(III.)

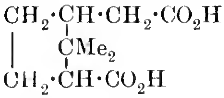
The latter inference is supported by the observation of Moycho and Zienkowski (*Annalen*, 1905, **340**, 54), that camphenilone does not form a hydroxymethylene compound, and hence possesses no methylene group adjacent to its carbonyl group. Stronger confirmation is afforded by the experiments of Bouveault and Blanc (*Compt. rend.*, 1908, **147**, 1314), who identified the product obtained by the action of sodamide on camphenilone as the amide of the acid:


,

which they also synthesised for the purpose of direct comparison.

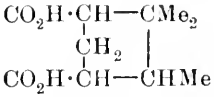
These experiments, considered alone, seem almost sufficient to establish the accuracy of Wagner's camphene formula. Yet whilst this is so, there is one branch of the recent work, and that not least in importance, in which the results cannot be reconciled so easily with the above camphene structure.

The fact that the chief product of the oxidation of camphene by alkaline permanganate is camphenic acid, which represents 80 per cent. of the yield by this method, cannot but be regarded as significant. The constitution of camphenic acid, $C_{10}H_{16}O_4$, which is isomeric with camphoric acid, has not yet been definitely determined. The configuration (IV) suggested by Wagner (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 680), and supported by Semmler, must now be finally abandoned, for an acid having this constitution has since been synthesised by Komppa (*Ber.*, 1911, **44**, 1536) from *apo*camphoric acid, and this is identical, not with camphenic acid, but with pinophanic acid:



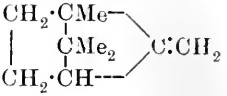
$$\begin{array}{lll} CH_2\cdot & CH\cdot CH_2\cdot CO_2H \\ \mid & \mid \\ \mid & CMe_2 \\ \mid & \mid \\ CH_2\cdot & CH\cdot CO_2H \end{array}$$

(IV.)



$$\begin{array}{lll} CO_2H\cdot & CH & —CMe_2 \\ & \mid & \mid \\ & CH_2 & \mid \\ & \mid & \mid \\ CO_2H\cdot & CH & —CHMe \end{array}$$

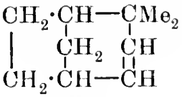
(V.)



(VI.)

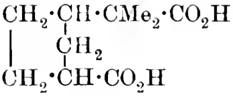
The formula (V) proposed by Moycho and Zienkowski (*loc. cit.*) has received no experimental confirmation, whilst Semmler's camphene formula (VI) seems incapable of providing any reasonable explanation other than that given by the formula (IV) of the production of such a compound as camphenic acid by oxidation (compare Henderson and Heilbron, Trans., 1911, **99**, 1901).

The question of the constitution of camphenic acid has received recent attention at the hands of Aschan (*Annalen*, 1910, **375**, 336), who, in order to render more easy of explanation the formation of an acid of this composition, proposed what is known as the "ethylene formula" (VII) for camphene, which is only a slight modification of Wagner's "methylene formula" (I):



$$\begin{array}{llll} CH_2\cdot & CH & — & CMe_2 \\ \mid & \mid & & \mid \\ \mid & CH_2 & & CH \\ \mid & \mid & & \| \\ CH_2\cdot & CH & — & CH \end{array}$$

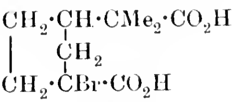
(VII.)



$$\begin{array}{ll} CH_2\cdot & CH\cdot CMe_2\cdot CO_2H \\ \mid & \mid \\ \mid & CH_2 \\ \mid & \mid \\ CH_2\cdot & CH\cdot CO_2H \end{array}$$

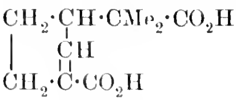
(VIII.)

This alternative formula leads to the structure (VIII) as representing the constitution of camphenic acid, to which Aschan lends his support. Moreover, he has studied the reactions of camphenic acid, and has succeeded in preparing several interesting derivatives and degradation products. The first of these is the monobromo-acid (IX), which does not appear to form a dibromide, but passes, on treatment with alkali, into an unsaturated acid (X) and a hydroxy-acid (XI), which does not form a lactone:



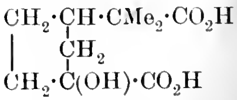
$$\begin{array}{ll} CH_2\cdot & CH\cdot CMe_2\cdot CO_2H \\ \mid & \mid \\ \mid & CH_2 \\ \mid & \mid \\ CH_2\cdot & CBr\cdot CO_2H \end{array}$$

(IX.)



$$\begin{array}{ll} CH_2\cdot & CH\cdot CMe_2\cdot CO_2H \\ \mid & \mid \\ \mid & CH \\ \mid & \| \\ CH_2\cdot & C\cdot CO_2H \end{array}$$

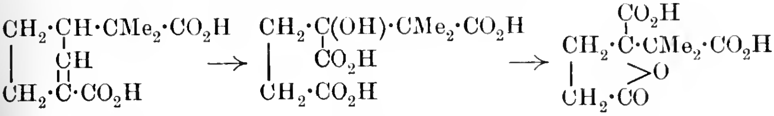
(X.)



$$\begin{array}{ll} CH_2\cdot & CH\cdot CMe_2\cdot CO_2H \\ \mid & \mid \\ \mid & CH_2 \\ \mid & \mid \\ CH_2\cdot & C(OH)\cdot CO_2H \end{array}$$

(XI.)

These facts argue for the presence of only one such grouping as $>CH\cdot CO_2H$ in camphenic acid. Still more important is the behaviour of dehydrocamphenic acid (X) towards nitric acid, oxidation taking place presumably at the double linking, accompanied by the substitution of a hydroxyl group for a tertiary hydrogen atom in the molecule, and by a loss of one carbon atom. The substance isolated has the composition $C_9H_{12}O_6$, and appears to be the lactone of a tribasic hydroxy-acid, $C_9H_{14}O_7$ (XII), a change which Aschan formulates in the following way:



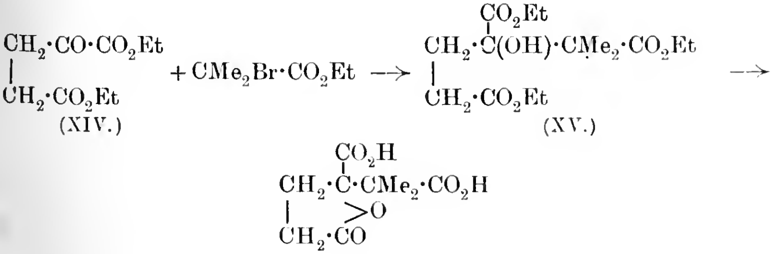
$$\begin{array}{l} CH_2\cdot CH\cdot CMe_2\cdot CO_2H \\ | \qquad \| \; CH \\ CH_2\cdot C\cdot CO_2H \end{array} \longrightarrow \begin{array}{l} CH_2\cdot C(OH)\cdot CMe_2\cdot CO_2H \\ | \qquad CO_2H \\ CH_2\cdot CO_2H \end{array} \longrightarrow \begin{array}{l} \qquad CO_2H \\ CH_2\cdot C\cdot CMe_2\cdot CO_2H \\ | \qquad >O \\ CH_2\cdot CO \end{array}$$

(X.) (XII.) (XIII.)

The γ-lactonic acid (XIII) melts at 254°, is very sparingly soluble in cold water or other solvents, and is remarkably stable towards nitric acid. No definite anhydride was obtained by Aschan, although he assumes that one is formed by the agency of acetic anhydride. Fusion of the lactonic acid with potassium hydroxide seems to confirm the formula (XIII), the products being succinic, *iso*butyric, and formic acids.

The authors of the present communication set out with the intention of synthesising not only camphenic acid itself, but also several of its degradation products, and if possible camphenilone (III), in order to test the validity of such reasoning concerning the constitution of camphene.

The first synthesis attempted was of the lactonic acid represented by formula (XIII), which was successfully accomplished by the following stages: ethyl α-ketoglutarate (XIV) was condensed in the presence of zinc with ethyl α-bromo*iso*butyrate, which gave rise to the hydroxy-ester (XV), distilling at about 215°/50 mm. Hydrolysis of this ester is effected by careful digestion with dilute acid, and the product isolated was found to be the γ-lactonic acid (XVI), which is the constitution assigned by Aschan to the acid (XIII):



$$\begin{array}{l} CH_2\cdot CO\cdot CO_2Et \\ | \\ CH_2\cdot CO_2Et \end{array} + CMe_2Br\cdot CO_2Et \longrightarrow \begin{array}{l} \qquad CO_2Et \\ CH_2\cdot C(OH)\cdot CMe_2\cdot CO_2Et \\ | \\ CH_2\cdot CO_2Et \end{array} \longrightarrow$$

(XIV.) (XV.)

$$\begin{array}{l} \qquad CO_2H \\ CH_2\cdot C\cdot CMe_2\cdot CO_2H \\ | \qquad >O \\ CH_2\cdot CO \end{array}$$

(XVI.)

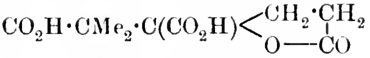
It will be readily agreed that the method of synthesis is such as to leave no doubt as to the constitution of the lactonic acid obtained; but even a superficial comparison of the properties of the synthetic acid with that derived by Aschan from camphenic acid suffices to show that the two acids are not identical. The synthetic lactonic acid melts sharply at 159° (95° lower than Aschan's acid), is very soluble in cold water, from which it does not crystallise, and on prolonged heating above its melting point changes into its anhydride, melting at 104°.

It is thus evident that the lactonic acid obtained by Aschan by the degradation of camphenic acid cannot have the constitution (XIII) which he assigns to it. The conclusiveness of the fusion experiment with potassium hydroxide is rather doubted by Aschan himself, as is evident from his own words: "Einiges Bedenken erregt der Umstand, dass das Schmelzen mit Kali tiefer eingreifender Natur ist und unter Umständen Umlagerungen herbeiführt."

It seems natural to suppose that the lactonic acid from camphenic acid contains a *gem*-dimethyl group, and is a γ-lactone formed from a tribasic acid possessing a tertiary hydroxyl group, and therefore must be a dimethyl derivative of the acid,

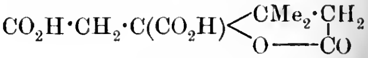
$$CO_2H{\cdot}\underset{\alpha}{CH_2}{\cdot}\underset{\beta}{C}(OH)(CO_2H){\cdot}\underset{\gamma}{CH_2}{\cdot}\underset{\delta}{CH_2}{\cdot}CO_2H,$$

in which the *gem*-dimethyl group occupies positions **α**, γ, or **δ**, instead of a methylene group. Of these three possible acids only two are at present known: the **α**-acid, the synthesis of which is described in this paper, and the γ-acid obtained by Perkin and Thorpe (Trans., 1901, **79**, 764), which decomposes at its melting point with loss of carbon dioxide.



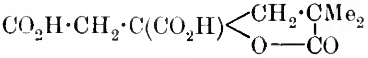
$$CO_2H{\cdot}CMe_2{\cdot}C(CO_2H){<}\begin{array}{l}CH_2{\cdot}CH_2\\ O\text{——}CO\end{array}$$

α (identical with XVI).



$$CO_2H{\cdot}CH_2{\cdot}C(CO_2H){<}\begin{array}{l}CMe_2{\cdot}CH_2\\ O\text{——}CO\end{array}$$

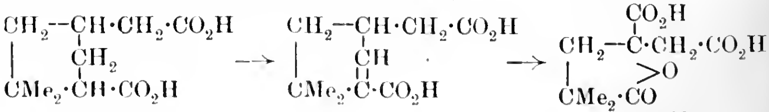
γ.



$$CO_2H{\cdot}CH_2{\cdot}C(CO_2H){<}\begin{array}{l}CH_2{\cdot}CMe_2\\ O\text{——}CO\end{array}$$

δ.

There remains, then, the only other alternative, namely, the **δ**-acid, and we are at present engaged in the difficult task of synthesising this acid, and desire therefore to reserve to ourselves this subject. Should the above lactonic acid prove to be identical with that of Aschan's, it would lead to the adoption of the following constitution for camphenic acid (XVII):



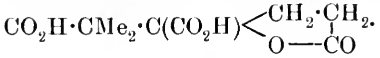
(XVII.)

(**δ**-Acid.)

There is, however, some ground for the suggestion that in the formation of camphenic acid from camphene we have another example of a profound internal rearrangement having taken place, such as was met with in the camphor molecule in the case of *iso*lauronolic acid.

EXPERIMENTAL.

*Condensation of Ethyl α-Ketoglutarate with Ethyl α-Bromo*iso*butyrate. Synthesis of the Lactonic Acid,*



$$CO_2H\cdot CMe_2\cdot C(CO_2H)<\begin{matrix} CH_2\cdot CH_2 \\ O\text{---}CO \end{matrix}.$$

The α-ketoglutaric acid required for this experiment was obtained from ethyl oxalosuccinate by imitating the procedure described by Wislicenus for its ketone hydrolysis (*Ber.*, 1911, **44**, 1564). We observed that the pure acid melted at 116°, and that it was readily esterified by means of 5 per cent. alcoholic hydrogen chloride on gently warming, yielding ethyl α-ketoglutarate as a colourless oil distilling at 165—168°/30 mm.

In a flask closed with a reflux condenser, the following quantities were mixed along with 200 c.c. of dry benzene: ethyl α-ketoglutarate (24 grams), granulated zinc (7·8 grams), and ethyl α-bromo*iso*butyrate (23·2 grams). The flask was heated on the steam-bath, and after some minutes a brisk ebullition took place, the reaction proceeding until all the zinc had disappeared. Some crystals of the solid zinc compound separated on cooling, and this was decomposed by the addition of ice and dilute sulphuric acid in the presence of a considerable volume of ether: the product was extracted with ether, washed with sodium hydrogen carbonate, dried, and the ether and benzene removed by distillation. The residue was subjected to careful distillation under diminished pressure, when practically no decomposition occurred, and the hydroxy-ester was obtained as a colourless or pale yellow oil distilling at 195—220°/50 mm., and on redistillation the boiling point 215°/50 mm. was observed:

0·1570 gave 0·3240 CO_2 and 0·1095 H_2O. C = 56·3; H = 7·8.
$C_{15}H_{26}O_7$ requires C = 56·6; H = 8·2 per cent.

The analysis indicates that this fraction consisted essentially of *ethyl β-hydroxy-αα-dimethylbutane-αβδ-tricarboxylate* (XV), which had been produced according to the scheme formulated on page 1977.

Hydrolysis.—The above hydroxy-ester was hydrolysed by boiling with 15 per cent. hydrochloric acid in a reflux apparatus, alcohol being allowed to escape from time to time by removing the air condenser. When all the oil had passed into solution, the latter was evaporated almost to dryness on the water-bath; the residue on cooling consisted of a solid, crystalline mass, which was drained on a porous tile and dried in a vacuum desiccator over solid potassium hydroxide, after which the crude crystals melted at about 145°. The substance was recrystallised several times from dry ether, in which it is sparingly soluble, and it then melted not very sharply at 154—155°; the analysis indicated that the substance was impure:

0·1166 gave 0·2166 CO_2 and 0·0605 H_2O. C=50·6; H=5·76.
$C_9H_{12}O_6$ requires C=50·0; H=5·55 per cent.

As the acid could not be further purified by repeated crystallisation, it was esterified by digesting for twelve hours with 8 per cent. alcoholic hydrogen chloride. The ester was isolated from the mixture in the usual way, and fractionated under diminished pressure, when it was obtained as a colourless, pleasant-smelling oil, distilling at 202°/25 mm., and an analysis showed it to be the diethyl ester of the lactonic acid, $C_9H_{12}O_6$.

This oil was now hydrolysed in the manner described above in the case of the hydroxy-ester, and when dried and recrystallised from dry ether, the pure compound separated in colourless, hard nodules, melting sharply at 159°:

0·1204 gave 0·2208 CO_2 and 0·0602 H_2O. C=50·0; H=5·6.
$C_9H_{12}O_6$ requires C=50·0; H=5·6 per cent.

The following titration experiments bear out the character of the substance as a dibasic lactonic acid of the constitution (XVI):

0·3442 gram required 31·62 c.c. of $N/10$-NaOH for neutralisation in the cold, whence equivalent=108·8. The calculated equivalent for the dibasic acid, $C_9H_{12}O_6$, is 108.

An excess of alkali was then added, amounting in all to 57 c.c. of $N/10$-NaOH, and the solution boiled for some minutes, allowed to cool, and titrated with $N/10$-H_2SO_4, when 10·9 c.c. of acid of this strength were required for neutralisation; the difference, 46·1 c.c., gives the total alkali, whence the new equivalent=75. The calculated equivalent for a tribasic acid, $C_9H_{14}O_7$, =78.

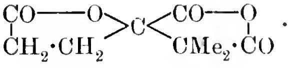
The *silver* salt is sparingly soluble in water, but on exposure to light is quickly discoloured:

0·1091 gave 0·0542 Ag. Ag=49·7.
$C_9H_{10}O_6Ag_2$ requires Ag=50·2 per cent.

The *calcium* salt, obtained by boiling the acid with water and calcium carbonate and concentrating the filtered solution, is very soluble in water, the syrupy liquid giving a glassy mass on cooling rapidly, and small stellate crystals when slowly cooled. The *barium* and *zinc* salts behave similarly. The *copper* salt is readily soluble, and separates as dark blue crystals on evaporation of its solution in a vacuum. On warming, however, the salt rapidly hydrolyses, and a pale blue basic salt is deposited.

The lactonic acid, $C_9H_{12}O_6$, dissolves readily even in cold water, and exhibits an exceptional degree of solubility in the usual organic solvents. It is best recrystallised from dry ether.

The Lactone Anhydride,



A melting-point determination of the lactonic acid having been made, the contents of the capillary tube were allowed to cool somewhat, and the molten substance induced to solidify by inserting a platinum wire; it was now observed that the crystals melted at 101° instead of 159°. A larger quantity of the crude lactonic acid was similarly heated in a test-tube immersed in a sulphuric acid bath, and maintained at a temperature of 165°. After some hours the whole of the substance, except a small, brown residue, had sublimed, forming colourless, glistening needles, which collected on the cooler walls of the tube; these were readily detached, and melted sharply at 104°. During the process of heating there was no evolution of carbon dioxide, and the analytical results indicated that the new substance was the anhydride of the lactonic acid, $C_9H_{12}O_6$:

0·1330 gave 0·2645 CO_2 and 0·0615 H_2O. $C=54·2$; $H=5·1$.
$C_9H_{10}O_5$ requires $C=54·5$; $H=5·1$ per cent.

The cost of this investigation has been defrayed by a grant from the research fund of the Chemical Society, which assistance the authors desire gratefully to acknowledge.

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CCXI.—*The Influence of Certain Salts on the Dynamic Isomerism of Ammonium Thiocyanate and Thiocarbamide.*

By William Ringrose Gelston Atkins and
Emil Alphonse Werner.

The experiments described in the present paper were carried out with two main objects in view: first, in the hope of obtaining some evidence likely to throw further light on the reversible isomerism of the above two compounds, and secondly, to ascertain if it is possible by the introduction of a new condition to disturb the normal equilibrium, and thus bring about a more complete conversion of ammonium thiocyanate into thiocarbamide than has hitherto been effected. Investigations of the change so far have proved that under the best conditions equilibrium is established when 25 per cent. of thiocarbamide, the less stable isomeride, has been produced. It is obvious from the study of the action of heat on thiocarbamide that any hope for success in this direction must lie in attempts to increase the stability of the compound at about 170° (the melting point of thiocarbamide when determined in the usual manner), a temperature at which thiocarbamide, under ordinary conditions, reverts with great rapidity until the equilibrium mixture is attained.

The comparatively high melting points of the compounds $(CSN_2H_4)_4,KI$ (189°: Werner, Proc., 1906, **22**, 245) and $(CSN_2H_4)_4,RbI$ (202°: Atkins and Werner, this vol., p. 1174) and other additive compounds seem to imply greater stability of the thiocarbamide in these substances, hence experiments have been made on the influence of different haloid salts of the alkali metals on the transformation of ammonium thiocyanate and thiocarbamide. Before describing the results which we have obtained, it may be stated at once that so far all attempts to increase the amount of thiocarbamide have been unsuccessful, and although the failure in this direction has been complete the results are nevertheless not without interest.

Experimental.

Action of Heat on Trithiocarbamide Potassium Thiocyanate.

The preparation of the compound $(CSN_2H_4)_3,KSCN$ (m. p. 143°) has already been described (Atkins and Werner, *loc. cit.*). It is analogous to the compound $(CSN_2H_4)_3,NH_4SCN$ (*loc. cit.*, m. p. 144°), which is produced in the equilibrium mixture already mentioned. This substance, however, changes during liquefaction, as the thiocarbamide reverts to ammonium thiocyanate. The following experiments were carried out to ascertain what effect was occasioned by the replacement of ammonium by potassium. The results in the subjoined table were obtained by heating at 174°, the thiocarbamide, estimated by Reynolds and Werner's method in portions withdrawn at intervals, being calculated as a percentage of that originally present in the compound, not on the total weight of the latter.

$t = 174°$.

Time, in minutes.	Thiocarbamide, per cent.	$k = 1/t \log a/a - x$.*
2	93·9	0·0157
7	77·0	0·0162
13	57·8	0·0183
23	40·6	0·0170
33	34·3	0·0140
43	26·7	0·0133
53	27·4	0·0106
90	25·5	—
	Mean of first five	0·0162

* There is a misprint in this formula in our previous paper.

It is clear that the reaction follows the unimolecular formula, although owing to the very great increase in velocity occasioned by small rises in temperature in this region the values of k are not in good agreement. The equilibrium percentage appears to be reached in about forty-five minutes, the value 27·4 per cent. lying slightly off the curve when the results are plotted; thus it may be seen that both in the time required to attain equilibrium and in the percentage composition of the resulting fusion (Reynolds and Werner, Trans., 1903, **83**, 3) the behaviour of this compound closely resembles that of pure thiocarbamide. The potassium thiocyanate present has practically no effect, for as soon as ammonium thiocyanate is formed, the compound $(CSN_2H_4)_3,NH_4SCN$ must be present in the fusion, although largely dissociated; the thiocarbamide in this then reverts further.

The Reversion of Thiocarbamide in the Tetrathiocarbamide Alkali Halogen Compounds.

The following experiments were carried out chiefly with the potassium iodide member of the series, $(CSN_2H_4)_4,KI$ (m. p. 189°). In dilute aqueous solution it is practically completely dissociated, as shown by the molecular-weight determinations here recorded, giving four thiocarbamide molecules and two ions of the salt.

Compound, per cent.	M.W.
2·12	77
5·73	78

Theory requires 78·3 for complete dissociation. Determinations in boiling ethyl alcohol give the following values:

Compound, per cent.	M.W.
2·19	81
4·39	96

Theory requires 94 for dissociation into thiocarbamide and potassium iodide, five molecules in all. Since this is so, it is to be expected that the reversion will be complete in aqueous solution, so it was not studied. It may here be remarked that thiocarbamide itself consists of simple molecules when in aqueous solution.

The high melting point of the compound $(CSN_2H_4)_4,KI$, namely, 189°, determined in the usual manner, as against 169° for thiocarbamide under similar conditions (we have already shown that the true melting point of the latter is about 200°), leads one to expect that its stability is greater than that of free thiocarbamide. The action of heat on the potassium compound gave results as follows:

SERIES I.

Temperature.	Time, in minutes.	Thiocarbamide, per cent.
142°	72	100·0
178	72	15·8
182	72	14·8
188	90	13·5
188	315	13·9

In the last two experiments the percentages recorded are corrected for loss by volatilisation. At the lower temperatures and shorter times this loss did not amount to 0·2 per cent., usually much less. It may be seen that, whilst at 142° the potassium compound is perfectly stable, whereas free thiocarbamide at this temperature reverts fairly rapidly, yet at the higher temperatures the reversion proceeds even further than with thiocarbamide alone, a state of equilibrium being reached at about 14 per cent. of the latter.

To determine this point more accurately, the compound $(CSN_2H_4)_4,KI$ was heated at 189° and at 184° for various lengths

SERIES II.—$t = 189°$.

$(CSN_2H_4)_4,KI$.

Thiocarbamide, per cent.	Time, in minutes.	$k = \frac{1}{t}\log\frac{a}{a-x}$.
43·4	10	
15·5	20	0·0447, between $t = 10$ and $t = 20$
15·0	30	
14·3	41	
14·4	50	
14·0	60	
14·4	70	
14·5	80	
13·7	100	

SERIES III.—$t = 184°$.

$(CSN_2H_4)_4,KI$.

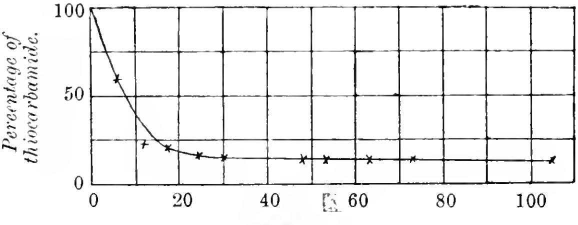
Thiocarbamide, per cent.	Time, in minutes.	k.
59·7	6	0·0373
20·8	18	0·0378
15·6	24	0·0336
14·1	30	—
13·7	48	—
13·3	53	—
13·6	63	—
13·6	73	—
12·1	105	—

of time, and the results are shown in Fig. 1; the data are given in Series II and III.

At 189° equilibrium was reached in about thirty minutes; the amount of thiocarbamide which remained was found to be 14·3 per cent. of that originally present, taking the mean value of Series II. It may be pointed out that the isomerides were then present in the ratio of one molecule of thiocarbamide to six of ammonium thiocyanate, and that there was 1 molecule of thiocarbamide to 2·03 molecules of potassium iodide, assuming that double decomposition had not occurred. Since, however, the reversion proceeds further in the case of the compound $(CSN_2H_4)_4,KI$ than in that of thiocarbamide, it seemed probable that this was due to double decomposition with the production of ammonium iodide and potassium thiocyanate. Experiments with the compound $(CSN_2H_4)_3,KSCN$, however, showed that in the latter case equilibrium was established when the normal 25 per cent. was present; thus it would appear that the further transformation was due to the amount of ammonium thiocyanate having diminished. Considering molecular proportions, however, it is seen that, assuming double decomposition to be complete, this explanation will not explain the results quantitatively, as out of every gram-molecule of the compound $(CSN_2H_4)_4,KI$ there remains more than 54 grams of ammonium thiocyanate above that accounted for both by the above assumption, and by the formation of the 25 per cent. equilibrium. So even allowing that the double decomposition has been complete, the equilibrium percentage of thiocarbamide is 18·9.

FIG. 1.

Temperature 184°.



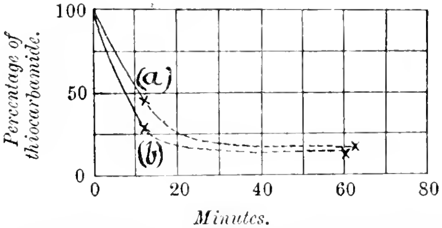
Decomposition of thiocarbamide in $(CSN_2H_4)_4,KI$.

In order to ascertain whether the potassium iodide compound alters the equilibrium percentage of thiocarbamide when the two are heated together, a mixture containing free thiocarbamide and the compound in the proportion of 3 grams of the former to one of the latter was maintained at 184° until equilibrium was reached. Calculating on the basis that the compound $(CSN_2H_4)_4,KI$ leaves only 14·3 per cent. of its thiocarbamide unchanged after heating, it was found that of the added thiocarbamide only 20·2 per cent. remained instead of 25 per cent. This result was confirmed in another experiment. The addition of potassium iodide to the compound $(CSN_2H_4)_4,KI$ so that the total salt was slightly in excess of the thiocarbamide only lowered the equilibrium position to 12·3 per cent. The temperature maintained in the previous experiments was 184°, as in Series III.

The results of the action of heat on the reversion of thiocarbamide in the compounds $(CSN_2H_4)_4,RbI$ and $(CSN_2H_4)_4,CsI$ are shown in Fig. 2. The details are given in Series IV. They furnish almost identical equilibrium percentages, namely, 16·9 and 16·6 respectively. The velocity-constant of the cæsium compound is slightly higher than that of the potassium member of the series at the same temperature, whilst that of the rubidium member is much lower. This may probably be taken as due to delay at the start owing to the much higher melting point of the latter substance.

Fig. 2.

Temperature 184°.



(a). *Decomposition of thiocarbamide in* $(CSN_2H_4)_4,RbI$.
(b). ,, ,, $(CSN_2H_4)_4,CsI$.

SERIES IV.—$t = 184°$.

$(CSN_2H_4)_4,RbI$ (m. p. 202°).			$(CSN_2H_4)_4,CsI$ (m. p. 191°).		
Thiocarbamide, per cent.	Time, in minutes.	k.	Thiocarbamide, per cent.	Time, in minutes.	k.
47·5	12	0·0269	29·3	12	0·0444
16·9	62	—	16·6	60	—

The Reversion of Thiocarbamide in the Presence of Alkali Halogen Salts.

Since potassium iodide alters the equilibrium percentage of thiocarbamide, it became advisable to study the influence of this salt on the velocity-constant of the reversion of the two isomerides. Accordingly, thiocarbamide and ammonium thiocyanate were heated alone and with the addition of one molecular proportion of iodide to form molecular proportions of each isomeride. The subjoined figures show that the rate of reversion of the non-saline isomeride was increased, whilst that of the saline isomeride was diminished. The temperature was maintained at 168°.

Composition.	*k*.	Composition.	*k*.
CSN_2H_4	0·0056	NH_4SCN	0·0037
$4CSN_2H_4+KI$	0·0074	$4NH_4SCN+KI$.....	0·0034

These increases and decreases were more marked when approximately the same molecular proportions of sodium iodide, $NaI,2H_2O$, were employed instead of potassium iodide. It was, moreover, found that all the thiocarbamide reverted when heated with a large excess of this sodium salt. As the reversion is known to be complete in aqueous solution, it was thought that the above behaviour might be due to the presence of water. Further experiments were therefore made with the anhydrous salt, and to include the entire series thiocarbamide was intimately mixed and heated with from seven to eleven times its weight of the chlorides, bromides, and iodides of potassium, sodium, and ammonium, until equilibrium had been attained with certainty at a temperature of 170°. The excess of salt being great in each case, the fluctuations in the proportions are not appreciable, for no correlation could be found between the percentages of thiocarbamide remaining and the excess taken. The table below shows the equilibrium percentages of thiocarbamide obtained in the presence of excess of the several salts.

Thiocarbamide per cent.—$t=170°$.

	Cl.	Br.	I.
K	12·89	12·24	9·04
Na..............	14·64	17·26	0·58
NH_4	19·57	21·70	12·43

When a small quantity of water was added to a mixture of potassium iodide and thiocarbamide similar to the one taken above, only 3·27 per cent. of the latter remained after heating.

A peculiar feature of the above table is the great difference between the effect produced by sodium iodide as compared with that of the other salts; thus, whilst reversion proceeds furthest in the presence of iodides, it is almost complete with the sodium salt. A larger percentage of thiocarbamide appears to persist with the bromides than with the chlorides, except for potassium, where the small difference is in favour of the chloride, and may be due to experimental error. It will also be noticed that, except in the case of sodium iodide, reversion to ammonium thiocyanate diminishes in the order: potassium, sodium, ammonium.

In the production of these equilibria two and possibly three factors are obviously concerned. Since equilibrium between thiocarbamide and ammonium thiocyanate is one between the molecules, and not directly between thiocarbamide and ammonium and thiocyanate ions, as is shown by the complete reversion of the non-saline isomeride in dilute aqueous solution, and by the decrease in thiocarbamide when water as well as potassium iodide was added to the fusion, it is clear that any cause which increases the degree of ionisation of ammonium thiocyanate in the fusion must alter the equilibrium percentage in favour of the latter isomeride. The addition of any salt appears to increase the ionisation, as double decomposition has already been shown (in the case of the compound $(CSN_2H_4)_4,KI$) to be by itself insufficient to explain the quantitative results obtained; thus, although double decomposition with the formation of partly undissociated chlorides, bromides, and iodides of ammonium and thiocyanates of sodium and potassium in the respective cases must lessen the amount of the saline isomeride and so disturb the normal 25 per cent. equilibrium, yet this in itself cannot explain the results; for when ammonium salts are added there can be no such exchange, since the only positive ion present is ammonium. Indeed, it is rather to be expected that the ionisation of ammonium thiocyanate would have been diminished by such an addition, but as the composition of the fusion has obviously changed, its properties as an ionising medium have probably changed also.

The third factor is the possibility of the occurrence of compounds such as $(CSN_2H_4)_4,MX$ undissociated in the fusion, thus probably increasing the stability of thiocarbamide and checking its reversion. In the case of the alkali chlorides, however, the existence of such compounds is so far only represented by $(CSN_2H_4)_4,NH_4Cl$ (m. p. 154°: Emerson Reynolds, Trans., 1891, **59**, 385), and hence this is probably not a factor of importance.

Preparation of Additive Compounds of Thiocarbamide with Saline Iodides.

The general procedure adopted in the preparation of the following compounds consisted in mixing hot alcoholic solutions of thiocarbamide and the saline iodide; in many cases the additive compound was directly produced and separated on cooling, whilst in a few instances, more particularly with the complex tertiary and quaternary iodides, it was found necessary to heat the solutions to boiling under a reflux condenser for fifteen minutes to an hour. In all cases the compounds were purified by recrystallisation from absolute alcohol before being analysed. The results obtained are as follows:

Thiocarbamide and Hydrazine Hydriodide.—The compound separated in a felted mass of long, slender needles, with satiny lustre, melting at 136°:

0·25 gave 0·068 I. I = 27·2.

$C_4H_{16}N_8S_4,N_2H_4,HI$ requires I = 27·37 per cent.

Thiocarbamide and Hydroxylamine Hydriodide.—This forms long, slender, silky needles, melting at 178°:

0·25 gave 0·0685 I. I = 27·4.

$C_4H_{16}N_8S_4,NH_2{\cdot}OH,HI$ requires I = 27·31 per cent.

Thiocarbamide and Aminoguanidine Hydriodide.—This compound separates in long, slender, hair-like needles with satiny lustre, melting at 174°:

0·25 gave 0·0628 I. I = 25·12.

$C_4H_{16}N_8S_4,CN_4H_6,HI$ requires I = 25·09 per cent.

Guanidine hydriodide did not form a compound.

Thiocarbamide and Pyridine Hydriodide.—It was found necessary to boil the alcoholic solution for half an hour. The compound separates in slender, glistening needles, melting at 157°:

0·25 gave 0·08826 I. I = 35·3.

$C_2H_8N_4S_2,C_5H_5N,HI$ requires I = 35·37 per cent.

Thiocarbamide and Pyridine Methiodide.—The compound is readily formed. It separates from alcoholic solution in slender, flat, lustrous prisms, melting at 144°:

0·25 gave 0·08509 I. I = 34·036.

$C_2H_8N_4S_2,C_5H_5N,MeI$ requires I = 34·04 per cent.

Thiocarbamide and Quinoline Hydriodide.—The compound is readily formed, and separates in minute rosettes of silky, yellow needles, melting at 137°:

0·25 gave 0·07874 I. I = 31·49.

$C_2H_8N_4S_2,C_9H_7N,HI$ requires I = 31·05 per cent.

Thiocarbamide and Quinoline Methiodide.—This compound forms very slender, silky needles melting at 134°, and resembling in appearance the characteristic form of tetrathiocarbamide derivatives:

0·25 gave 0·0757 I. I = 30·28.

$C_2H_8N_4S_2,C_9H_7N,MeI$ requires I = 30·02 per cent.

Thiocarbamide and Quinoline Ethiodide.—This compound separates in bright, canary-yellow prisms, melting at 126°. After two recrystallisations:

0·25 gave 0·88 I. I = 35·2.

$C_2H_4N_2S_2,C_9H_7N,EtI$ requires I = 35·18 per cent.

Thiocarbamide and Trimethylethylammonium Iodide.—This compound separated in slender, glistening prisms, melting at 141°, after the alcoholic solution of the components had been boiled for half-an-hour:

0·25 gave 0·08763 I. I = 35·05.

$C_2H_8N_4S_2,NMe_3EtI$ requires I = 34·6 per cent.

Thiocarbamide and Tripropylamine Hydriodide.—This compound separates in microscopic, silky needles, melting at 166°:

0·25 gave 0·075 I. I = 30·0.

$C_2H_8N_4S_2,N(C_3H_7)_3HI$ requires I = 30·02 per cent.

Thiocarbamide and Methyltripropylammonium Iodide.—This compound separates in stout prisms or slender needles depending on the concentration. It melts at 128°:

0·25 gave 0·073 I. I = 29·2.

$C_2H_8N_4S_2,N(C_3H_7)_3MeI$ requires I = 29·06 per cent.

Thiocarbamide and Triethylpropylammonium Iodide.—This compound forms slender, brittle, needle-like crystals, melting at 165°:

0·25 gave 0·074 I. I = 29·6.

$C_2H_8N_4S_2,NEt_3(C_3H_7)I$ requires I = 30·02 per cent.

Thiocarbamide and Phenyldimethylethylammonium Iodide.—This compound separates in stout, truncated prisms, which melt at 112°, and at a higher temperature readily decompose, giving mercaptan:

0·25 gave 0·07366 I. I = 29·46.

$C_2H_8N_4S_2,NPhMe_2EtI$ requires I = 29·60 per cent.

Tetramethylammonium iodide and thiocarbamide were boiled together in alcoholic solution for two hours, but not a trace of a compound was formed. The iodine was estimated in all the above compounds by boiling with an excess of ferric sulphate in strong solution, and titration of the liberated iodine with *N*/10-sodium thiosulphate.

The above series of compounds was prepared in order to obtain data regarding the ratio in which thiocarbamide unites directly with saline iodides of different constitution.

It is noteworthy that although aminoguanidine hydriodide unites readily with thiocarbamide, no compound was obtained with guanidine hydriodide. The compound $(CSN_2H_4)_2,NEt_4I$ (m. p. 135°) was prepared by Emerson Reynolds (Trans., 1891, **59**, 388). We have not been able to obtain any compound with tetramethylammonium iodide, which thus behaves like sodium iodide, in exhibiting no tendency to unite with thiocarbamide (Werner, Proc., 1906, **22**, 245); the displacement of one methyl group by ethyl, however, is sufficient to enable a compound to be formed.

Whilst the simple ammonium bases and primary amines (see Emerson Reynolds, *loc. cit.*) form tetrathiocarbamide derivatives, the tertiary amines and quaternary bases appear to always produce dithiocarbamide compounds.

We have obtained one exception to the latter rule, namely, the compound CsN_2H_4,C_9H_7N,C_2H_5I (m. p. 126°).

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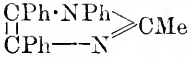
CCXII.—*The Condensation of α-Keto-β-anilino-αβ-diphenylethane and its Homologues with Ethyl Chlorocarbonate and Thionyl Chloride.*

By HAMILTON McCOMBIE and JOHN WILFRID PARKES.

EVEREST and McCombie (Trans., 1911, **99**, 1746) have described a method for the preparation of glyoxalines from acyl derivatives of α-keto-β-anilino-αβ-diphenylethane. By heating these derivatives with concentrated ammonia under pressure, these investigators found that glyoxalines were produced; thus, α-keto-β-acetylanilino-αβ-diphenylethane (I), when heated in a sealed tube with ammonia, was found to yield 1:4:5-triphenyl-2-methylglyoxaline (II):

$COPh{\cdot}CHPh{\cdot}NPhAc$

(I.)



$$\begin{array}{l} \mathrm{CPh{\cdot}NPh} \\ \| \\ \mathrm{CPh{-}{-}N} \end{array}\!\!>\!\mathrm{CMe}$$

(II.)

$COPh{\cdot}CHPh{\cdot}NPh{\cdot}CO_2Et$

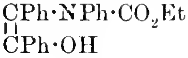
(III.)

The attempt has now been made to extend this reaction to another acyl derivative, namely, the carbethoxy-derivative. This compound (III) was prepared by the action of ethyl chlorocarbonate on α-keto-β-anilino-αβ-diphenylethane. It was found that no glyoxaline was formed when this carbethoxy-compound was heated with ammonia, but that 2-keto-3:4:5-triphenyl-2:3-dihydro-oxazole (IV) was obtained. In this case the ammonia acts merely as a hydrolysing agent. The same reaction can be brought about more conveniently by the action of potassium hydroxide in alcoholic solution on the carbethoxy-compound.

The mechanism of the reaction is probably as follows: The carbethoxy-derivative, in presence of a small quantity of alkali, gives a strong, yellow coloration, behaving in this respect similarly to the other acyl derivatives of α-keto-β-anilino-αβ-diphenylethane (Everest and McCombie, *loc. cit.*, p. 1748); this is doubtless due to its existence in the tautomeric enolic form (V). Alcohol is then eliminated between the carbethoxy-group and the hydroxyl group, resulting in the formation of the oxazole (IV):

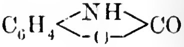
$\begin{array}{l}\mathrm{CPh\cdot NPh}\\ \Vert \\ \mathrm{CPh—O}\end{array}\!\!>\mathrm{CO}$

(IV.)



$\begin{array}{l}\mathrm{CPh\cdot NPh\cdot CO_2Et}\\ \Vert \\ \mathrm{CPh\cdot OH}\end{array}$

(V.)



$\mathrm{C_6H_4}\!<\!\begin{array}{c}\mathrm{NH}\\ \mathrm{O}\end{array}\!\!>\mathrm{CO}$

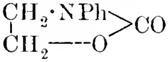
(VI.)

The possibility of the formation of an oxazole by this method of synthesis depends largely on the ease of removal of the two hydrogen atoms from α-keto-β-anilino-αβ-diphenylethane.

If this conception of the reaction be correct, then it should be possible to form the oxazole in one step by the action of carbonyl chloride on α-keto-β-anilino-αβ-diphenylethane. This was achieved successfully by the employment of pyridine as the agent for the removal of the hydrogen chloride.

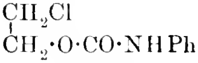
This method for the preparation of the dihydro-oxazoles is analogous to the reactions for the preparation of dihydrobenzoxazole described by Chelmicki (*Ber.*, 1887, **20**, 177) and Jacoby (*J. pr. Chem.*, 1888, [ii], **37**, 39). These investigators, by the action of ethyl chlorocarbonate or carbonyl chloride on *o*-aminophenol, were enabled to prepare 1-keto-1:2-dihydrobenzoxazole (VI).

Another analogous reaction is the preparation of 2-keto-3-phenyl-2:3:4:5-tetrahydro-oxazole (VII). Nemirowski (*J. pr. Chem.*, 1885, [ii], **31**, 175) obtained this compound by the elimination of hydrogen chloride from the β-chloroethyl ester of phenylcarbamic acid (VIII), whilst Otto (*J. pr. Chem.*, 1891, [ii], **44**, 17) obtained it by the action of carbonyl chloride on α-hydroxy-β-anilinoethane (IX):



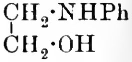
$\begin{array}{l}\mathrm{CH_2\cdot NPh}\\ | \\ \mathrm{CH_2—O}\end{array}\!\!>\mathrm{CO}$

(VII.)



$\begin{array}{l}\mathrm{CH_2Cl}\\ | \\ \mathrm{CH_2\cdot O\cdot CO\cdot NHPh}\end{array}$

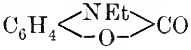
(VIII.)



$\begin{array}{l}\mathrm{CH_2\cdot NHPh}\\ | \\ \mathrm{CH_2\cdot OH}\end{array}$

(IX.)

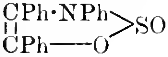
The dihydro-oxazoles described in this communication are extremely stable. Boiling with dilute acids has no effect, and attempts to reduce the compounds with sodium amalgam in alcoholic solution were unsuccessful. The basicity of the compounds is so slight that no hydrochloride, picrate, or platinichloride could be isolated. This anomalous behaviour of these compounds can be traced, probably, to the presence of the three phenyl groups in the molecule. Not only do these groups protect the ring from attack by reagents, but also the acidic nature of the phenyl group asserts itself, and renders the compounds practically neutral. Several attempts were made to attack the carbonyl group in the molecule, but they were all fruitless. Phosphorus pentachloride, aniline, and phenylhydrazine were all without action on the oxazoles. This failure to obtain a compound with aniline is all the more remarkable since Seidel (*J. pr. Chem.*, 1890, [ii], **42**, 450) was able to prepare a condensation product from aniline and 1-keto-2-ethyl-1:2-dihydro-oxazole (X):



$$C_6H_4{<}\begin{matrix}NEt\\ -O-\end{matrix}{>}CO$$

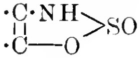
(X.)

We describe, also, in this communication, the products which can be obtained from α-keto-β-anilino-$\alpha\beta$-diphenylethane by substituting thionyl chloride for carbonyl chloride. It has been shown by Michaelis (*Ber.*, 1895, **28**, 1016; 1896, **29**, 710) that thionyl chloride reacts with secondary amines; thus, from diethylamine and thionyl chloride he was able to obtain thionyldiethylamine, $SO(NHEt_2)_2$. Further, it is well known that thionyl chloride reacts with alcohols to form the esters of sulphurous acid. Now, in the enolic form of α-keto-β-anilino-$\alpha\beta$-diphenylethane, there are present, at one and the same time, a hydroxyl group and a secondary amino-group. The thionyl chloride reacts with both these groups, two molecules of hydrogen chloride are eliminated, and the resulting product has the constitution (XI). In other words, we obtained a compound similar to the oxazoles, but having the CO-group of these compounds replaced by the SO-group. The authors propose to call this new heterocyclic ring (represented by formula XII) the oxasulphinazole ring, indicating by this name the relationship which this ring bears to the sulphinic acids on the one hand, and the oxazoles on the other. Adopting for this ring a numbering similar to that in use for the oxazoles, compound (XI) would be 3:4:5-triphenyloxasulphinazole.



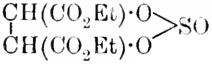
$$\begin{matrix}CPh\cdot NPh\\ \|\\ CPh—O\end{matrix}{>}SO$$

(XI.)



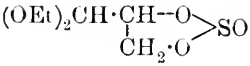
$$\begin{matrix}\cdot C\cdot NH\\ \|\\ \cdot C—O\end{matrix}{>}SO$$

(XII.)



$$\begin{matrix}CH(CO_2Et)\cdot O\\ |\\ CH(CO_2Et)\cdot O\end{matrix}{>}SO$$

(XIII.)



$$(OEt)_2CH\cdot\begin{matrix}CH—O\\ |\\ CH_2\cdot O\end{matrix}{>}SO$$

(XIV.)

Schiller (*Ber.*, 1909, **42**, 2017) describes a ring compound (XIII) which is formed by the action of thionyl chloride on ethyl tartrate. In the same paper, Schiller refers to a dissertation (Moers, *Berlin*, 1907), in which is described a thionyl compound of glycerolacetal (XIV).

The oxasulphinazoles described in this communication are yellow solids, soluble in alcohol and in most other organic solvents. They are not as stable as the oxazoles described above, for the ring is broken by boiling the substance with concentrated aqueous potassium hydroxide, and yields α-keto-β-anilino-$\alpha\beta$-diphenylethane. All the sulphinazoles give a dark emerald-green coloration when treated with a drop of concentrated sulphuric acid.

Attempts were also made to obtain compounds analogous to the oxazoles and the sulphinazoles by substituting sulphuryl chloride for carbonyl chloride and thionyl chloride. The condensation was attempted in pyridine solution, but, even in dilute solutions, no compounds containing sulphur were obtained. Compounds containing chlorine resulted, so that evidently the only effect of the sulphuryl chloride was to act as a chlorinating agent. The compounds were quite stable towards alkalis, and, as they were not identical with the compounds of benzoin and the chloroanilines, which have been prepared in this laboratory, it is probable that chlorination of the amine portion of the molecule had not taken place, but that the chlorine had entered one of the other benzene nuclei.

EXPERIMENTAL.

α-Keto-β-carbethoxyanilino-αβ-diphenylethane (III).

Five grams of α-keto-β-anilino-αβ-diphenylethane were shaken with a slight excess of ethyl chlorocarbonate (2·5 grams) and a 5 per cent. solution of sodium hydrogen carbonate (30 c.c.). The reaction was known to be finished when no traces of yellow were observed in the white, pasty mass. The solid product was separated, washed, and crystallised from absolute alcohol, when it crystallised in colourless prisms melting at 102°. The yield was 3·5 grams:

0·1050 gave 0·2956 CO_2 and 0·0565 H_2O. C = 76·78; H = 5·98.
0·3544 ,, 12·5 c.c. N_2 at 16·3° and 745·5 mm. N = 4·02.
$C_{23}H_{21}O_3N$ requires C = 76·88; H = 5·84; N = 3·9 per cent.

The alcoholic solution of this compound gives a yellow coloration on the addition of a drop of alkali, but this coloration is destroyed by neutralising the solution with acid.

2-*Keto*-3 : 4 : 5-*triphenyl*-2 : 3-*dihydro-oxazole* (IV).

This substance was prepared initially by heating equal weights of concentrated ammonia (D 0·880) and α-keto-β-carbethoxyanilino-αβ-diphenylethane in a sealed tube for seven to eight hours at 210—220°.

It was, however, prepared more readily by heating the carbethoxy-compound for half an hour in alcoholic solution with one and a-half molecular proportions of potassium hydroxide. The product was poured into water, acidified, and the solid which separated was crystallised from absolute alcohol. It separated in long, shining needles, melting at 210°. The yield was 80 per cent. of the theoretical.

The oxazole was also synthesised by mixing together a toluene solution of α-keto-β-anilino-$\alpha\beta$-diphenylethane (5 grams) with a 10 per cent. solution of carbonyl chloride in toluene. The yield (2 grams) was very poor, owing to the formation of the hydrochloride of α-keto-β-anilino-$\alpha\beta$-diphenylethane.

0·1035 gave 0·3051 CO_2 and 0·0464 H_2O. C=80·39; H=4·98.
0·3388 ,, 13·05 c.c. N_2 at 18° and 765·7 mm. N=4·48.
$C_{21}H_{15}O_2N$ requires C=80·51; H=4·79; N=4·47 per cent.

The compound was very soluble in benzene, but only moderately so in alcohol. Contrary to the general character of the oxazoles, the stability of this compound is very great. In the method of preparation it is subjected to the action of alcoholic potassium hydroxide, and it is recovered unchanged after boiling for several hours with acids. The ring is not broken by boiling with alcohol. The carbonyl group in the molecule does not react with either aniline or phenylhydrazine, even when the compounds are heated together in a sealed tube for seven to eight hours at 170—180°: neither could the group be attacked by phosphorus pentachloride.

The compound is so feebly basic that all attempts to isolate a hydrochloride from alcoholic, ethereal, or acetic acid solutions were unsuccessful, and no compound could be obtained with platinic chloride.

The conversion of the oxazole into the corresponding glyoxaline by heating it with concentrated ammonia in a sealed tube at a temperature of 300° could not be effected.

Numerous attempts were made to carry out the reduction of the oxazole with sodium amalgam in alcoholic solution. Experiments were tried with 3, 6, and 25 per cent. amalgams, but no definite results were obtained. The compound was either recovered unchanged, or the reduction proceeded to dibenzyl.

α-Keto-β-o-toluidino-$\alpha\beta$-diphenylethane, $COPh\cdot CHPh\cdot NH\cdot C_6H_4Me$.

Bandrowski (*Monatsh.*, 1888, **9**, 693) states that he obtained this compound by heating together at 150° molecular quantities of benzoin and *o*-toluidine for three-quarters of an hour. He states that, when recrystallised from absolute alcohol, the substance crystallised in needles melting at 141°.

We have repeated these experiments, but have been unable to prepare a product with this melting point. We have obtained the compound, however, by heating the two substances for one and a-half hours to a temperature of 130—140°. It was crystallised from methyl alcohol (it was found to be too soluble in absolute alcohol), when it separated in large, diamond-shaped crystals, melting at 80°:

0·2029 gave 0·6215 CO_2 and 0·1139 H_2O. C = 83·52; H = 6·24.*
0·2977 „ 12·10 c.c. N_2 at 13° and 751 mm. N = 4·72.
$C_{21}H_{19}ON$ requires C = 83·72; H = 6·31; N = 4·65 per cent.

The *hydrochloride*, $C_{21}H_{19}ON,HCl$, prepared in hot benzene solution, crystallises from acetone in colourless crystals melting at 170°: †

0·2042 gave 0·0880 AgCl. Cl = 10·66.
$C_{21}H_{19}ON,HCl$ requires Cl = 10·52 per cent.

α-*Keto-β-carbethoxy*-o-*toluidino-αβ-diphenylethane*, $C_{24}H_{23}O_3N$.

This compound was prepared by the action of ethyl chlorocarbonate, and crystallises from alcohol in small, colourless plates, melting at 96°:

0·1002 gave 0·2832 CO_2 and 0·0574 H_2O. C = 77·08; H = 6·35.
0·3018 „ 10·1 c.c. N_2 at 20° and 752 mm. N = 3·81.
$C_{24}H_{23}O_3N$ requires C = 77·2; H = 6·17; N = 3·75 per cent.

2-*Keto*-4:5-*diphenyl*-3-o-*tolyl*-2:3-*dihydro-oxazole*, $C_{22}H_{17}O_2N$.

This compound was prepared from the carbethoxy-derivative by the action of alcoholic potassium hydroxide. It crystallises from absolute alcohol in colourless prisms melting at 149°:

0·1045 gave 0·3095 CO_2 and 0·0526 H_2O. C = 80·77; H = 5·59.
0·4605 „ 16·7 c.c. N_2 at 20° and 758 mm. N = 4·21.
$C_{22}H_{17}O_2N$ requires C = 80·73; H = 5·2; N = 4·28 per cent.

α-*Keto-β*-m-*toluidino-αβ-diphenylethane*, $C_{21}H_{19}ON$.

This compound was prepared by heating benzoin (25 grams) with *m*-toluidine (12 grams) at 150° for twelve hours. The yellow product was crystallised from alcohol, when it separated in small, yellow crystals, melting at 123°. The yield was 23 grams:

0·1046 gave 0·3222 CO_2 and 0·0609 H_2O. C = 84·0; H = 6·47.
$C_{21}H_{19}ON$ requires C = 83·72; H = 6·31 per cent.

The *hydrochloride*, $C_{21}H_{19}ON,HCl$, was prepared in ethereal solution, and crystallises from glacial acetic acid in colourless crystals melting at 208°:

0·2212 gave 0·0931 AgCl. Cl = 10·41.
$C_{21}H_{19}ON,HCl$ requires Cl = 10·52 per cent.

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* For this analysis, we are indebted to Mr. S. A. Brazier, M.Sc.

† The hydrochloride of the corresponding para-compound is described in the literature, but no melting point is given. We prepared a specimen in benzene solution, and found that it melted at 198°.

*α-Keto-β-carbethoxy-*m*-toluidino-αβ-diphenylethane*, $C_{24}H_{23}O_3N$.

This substance crystallises from alcohol in small, colourless prisms, melting at 108°:

0·4584 gave 15·1 c.c. at 14·5° and 744·7 mm. N = 3·79.
$C_{24}H_{23}O_3N$ requires N = 3·75 per cent.

2-*Keto*-4 : 5-*diphenyl*-3-m-*tolyl*-2 : 3-*dihydro-oxazole*, $C_{22}H_{17}O_2N$.

This compound crystallises from alcohol in long, shining needles, melting at 203°:

0·1040 gave 0·3075 CO_2 and 0·0502 H_2O. C = 80·64 ; H = 5·42.
$C_{22}H_{17}O_2N$ requires C = 80·73 ; H = 5·2 per cent.

*α-Keto-β-carbethoxy-*p*-toluidino-αβ-diphenylethane*, $C_{24}H_{23}O_3N$.

This substance separates from alcohol in colourless prisms melting at 133°:

0·1026 gave 0·2901 CO_2 and 0·0577 H_2O. C = 77·08 ; H = 6·25.
0·3888 ,, 13·2 c.c. N_2 at 12° and 736 mm. N = 3·88.
$C_{24}H_{23}O_3N$ requires C = 77·2 ; H = 6·17 ; N = 3·75 per cent.

2-*Keto*-4 : 5-*diphenyl*-3-p-*tolyl*-2 : 3-*dihydro-oxazole*, $C_{22}H_{17}O_2N$.

This compound crystallises from alcohol in long, shining needles, melting at 227°:

0·1011 gave 0·2991 CO_2 and 0·0509 H_2O. C = 80·69 ; H = 5·57.
$C_{22}H_{17}O_2N$ requires C = 80·73 ; H = 5·2 per cent.

3 : 4 : 5-*Triphenyloxasulphinazole* (XI).

This compound was prepared by adding thionyl chloride (3 grams) in toluene (25 grams) to a solution of α-keto-β-anilino-αβ-diphenylethane (5 grams) dissolved in pyridine (25 grams). The mixture was allowed to remain overnight, and was then poured into dilute hydrochloric acid. The toluene was removed, the solid separated, and recrystallised from light petroleum or absolute alcohol, when it formed a yellow powder melting at 128°:

0·2128 gave 0·5607 CO_2 and 0·0883 H_2O. C = 71·8 ; H = 4·61.
0·3322 ,, 12·4 c.c. N_2 at 11·5° and 736 mm. N = 4·30.
0·2872 ,, 0·2059 $BaSO_4$. S = 9·83.
$C_{20}H_{15}O_2NS$ requires C = 72·08 ; H = 4·51 ; N = 4·20 ;
S = 9·61 per cent.

This oxasulphinazole is moderately soluble in most organic solvents. On boiling it with concentrated aqueous potassium hydroxide, α-keto-β-anilino-αβ-diphenylethane is regenerated. With a drop of concentrated sulphuric acid, the sulphinazole gives a dark emerald-green coloration.

4:5-*Diphenyl*-3-m-*tolyloxasulphinazole*, $C_{21}H_{17}O_2NS$.

When crystallised from alcohol, this compound separates as a yellow powder melting at 102°:

0·1775 gave 0·4708 CO_2 and 0·0763 H_2O. C=72·50; H=4·79.
0·2738 „ 0·1908 $BaSO_4$. S=9·55.
$C_{21}H_{17}O_2NS$ requires C=72·63; H=4·9; S=9·22 per cent.

4:5-*Diphenyl*-3-p-*tolyloxasulphinazole*, $C_{21}H_{17}O_2NS$.

When crystallised from alcohol or light petroleum, this compound separates as a yellow powder melting at 134°:

0·1855 gave 0·4930 CO_2 and 0·0805 H_2O. C=72·47; H=4·82.
0·2812 „ 0·1893 $BaSO_4$. S=9·23.
$C_{21}H_{17}O_2NS$ requires C=72·63; H=4·9; S=9·22 per cent.

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CCXIII.—*A Study of Some Dicyclic Quaternary Ammonium Compounds.*

By John Gunning Moore Dunlop.

I.

The Thermal Decomposition of 1:1-*Trimethylenepiperidinium Hydroxide.*

A considerable amount of time has been devoted by various chemists to the investigation of the products of decomposition formed when different types of quaternary ammonium hydroxides are distilled.

The results of the work hitherto done point to the following two general types of decomposition:

A. Elimination of an alkyl group as an alcohol or as an unsaturated hydrocarbon, with formation of a tertiary amine. This occurs in the case of open-chain, but rarely in that of cyclic quaternary ammonium hydroxides. (For a summary of these results, see J. von Braun, *Annalen*, 1911, **382**, 1; 1912, **386**, 273; see also Feer and Konigs, *Ber.*, 1885, **18**, 2393 for the decomposition of 1:1-dimethyltetrahydroquinolinium hydroxide.) The decomposition of diethylenedipiperidinium hydroxide into ethylenedipiperidine (Brühl, *Ber.*, 1871, **4**, 741) may be considered as a case of this type.

B. Rupture of the ring in cyclic quaternary ammonium hydroxide, with elimination of water only, and formation of an unsaturated amine, for example, the decomposition of 1 : 1-dimethylpiperidinium hydroxide (Hofmann, *Ber.*, 1881, **14**, 660).

It occurred to the present author, when engaged on the study of certain dicyclic quaternary ammonium salts (compare Jones and Dunlop, this vol., p. 1748) that it might be of interest to examine the products of decomposition in the case of 1 : 1-trimethylenepiperidinium hydroxide,

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>N(OH)<\begin{matrix}CH_2\\ CH_2\end{matrix}>CH_2,$$

the preparation of which is described by Gabriel and Stelzner (*Ber.*, 1896, **29**, 2583). This decomposition promised to be of the more interest in view of the remarkable results obtained by Gabriel and Colman (*Ber.*, 1906, **39**, 2875) on distilling a solution of the chloride of this radicle with concentrated potassium hydroxide, the principal product of this reaction being dipiperidyldipropyl ether, $C_5H_{10}N\cdot[CH_2]_3\cdot O\cdot[CH_2]_3\cdot NC_5H_{10}$.

The bromide and chloride of this base were prepared by Gabriel and Stelzner (*loc. cit.*), but both these were found to be too hygroscopic to admit of analysis. It was thought by the author that the iodide might prove to be an easier substance to handle, and it was decided to prepare it. The salt, γ-iodopropylpiperidinium hydriodide, was described by Gabriel and Colman (*loc. cit.*), but they did not convert the base of this salt into 1 : 1-trimethylenepiperidinium iodide. This was found to be a very easy process, and the iodide was obtained in fine crystals, of which a satisfactory analysis was made.

Distillation of the hydroxide obtained from this salt yielded an oil which exhibited the properties of a tertiary amine, combining readily with alkyl haloids, giving in particular a finely crystalline salt with benzyl iodide.

The base also reacted with acetyl and benzoyl chlorides, thus showing the presence of the hydroxyl group, and it appeared on consideration that the substance was probably γ-hydroxypropylpiperidine, $C_5H_{10}N\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$. The latter base was unknown, but was prepared by the action of trimethylenechlorohydrin on piperidine, and was proved to be identical with the decomposition product of 1 : 1-trimethylenepiperidinium hydroxide, yielding the same compounds as the latter with benzyl iodide and with benzoyl chloride.

During this decomposition a small proportion of piperidine is also formed, as is shown by the production of benzoylpiperidine when the product of distillation is benzoylated by the Schotten-Baumann method. The quantity of piperidine produced in this way is so minute that it was not found possible to identify the other product of the particular reaction by which the piperidine is formed. It is, however, surmised that this substance is probably allyl alcohol.

This type of decomposition of a quaternary ammonium hydroxide into a tertiary amine containing hydroxyl has never previously been recorded, and appears to be unique.

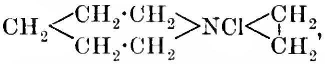
The formation of piperidine is also of interest, since in this reaction again the decomposition differs from that which is normal for quaternary alkylpiperidinium hydroxides, as there is no fission of the piperidine ring.

II.

The Action of Heat on β-Chloroethylpiperidine.

Marckwald and Frobenius (*Ber.*, 1902, **34**, 3557) found that the action of heat on β-chloroethylpiperidine, $C_5H_{10}N\cdot CH_2\cdot CH_2Cl$, is to give a mixture of two salts, one of which is crystalline and sparingly soluble in alcohol, whilst the other is a syrup from which they were unable to prepare any crystalline derivative, and with the examination of which they did not proceed further.

The crystalline compound proved on examination to be a quaternary ammonium salt, and, on the evidence alone of the method of its formation from β-chloroethylpiperidine, they assigned to it the structural formula:

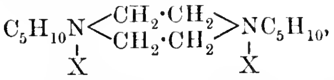


$$CH_2{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}NCl{<}\begin{matrix}CH_2\\ |\\ CH_2\end{matrix},$$

that is, 1:1-ethylenepiperidinium chloride (compare the formation of 1:1-trimethylenepiperidinium bromide from γ-bromopropylpiperidine, Gabriel and Stelzner, *loc. cit.*).

The present author, having been engaged for some time on the investigation of the bicyclic trimethylenepiperidinium compounds, was struck by the remarkable difference between the properties of the latter compounds and the so-called 1:1-ethylenepiperidinium salts. The trimethylenepiperidinium haloids are characterised by great solubility in alcohol, and the iodide melted at 175°. The salt obtained by Marckwald and Frobenius, and the corresponding iodide prepared by the present author, are very sparingly soluble in alcohol, and the iodide melts at 330°.

It appeared very unlikely that the difference of one methylene group in compounds of a similar type could produce so great a difference of solubility and melting point, and it was found on more careful examination that the compounds in question are really haloids of diethylenedipiperidine,



$$C_5H_{10}\underset{X}{N}\left<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\right>\underset{X}{N}C_5H_{10},$$

of which the bromide was described by Brühl (*Ber.*, 1871, **4**, 741) and the iodide by Aschan (*Ber.*, 1899, **31**, 991).

The identity of the compounds was further proved by the preparation from each of the aurichloride, which was described by Marckwald and Frobenius (*loc. cit.*). These proved to be identical in all respects, and each melted at 274°.

It still remained possible that the syrup which also resulted from the action of heat on β-chloroethylpiperidine was 1:1-ethylenepiperidinium chloride. It was accordingly treated with silver oxide and distilled. The distillate as in the case of the decomposition of diethylenedipiperidine dihydroxide (Brühl, *loc. cit.*), consisted mainly of ethylenedipiperidine, as was proved by the preparation therefrom of the dibenzyl iodide, which was identical with the corresponding derivative of ethylenedipiperidine synthesised in the usual way.

Since the results described in the earlier part of this paper suggest that 1:1-ethylenepiperidinium hydroxide should give, when heated, β-hydroxyethylpiperidine, it is improbable that this syrup is 1:1-ethylenepiperidinium chloride.

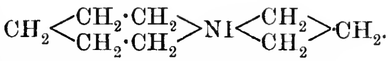
It is therefore clear that Marckwald and Frobenius were wrong in concluding that the action of heat on β-chloroethylpiperidine is to give 1:1-ethylenepiperidinium chloride, and no evidence appears at present to have been produced for the existence of this compound.

EXPERIMENTAL.

I.

γ-Iodopropylpiperidine, $C_5H_{10}N\cdot CH_2\cdot CH_2\cdot CH_2I$.

This base is obtained by the action of potassium hydroxide on its hydriodide (Gabriel and Colman, *loc. cit.*), and is converted, when heated on the water-bath, into 1:1-*trimethylenepiperidinium iodide*,



$$CH_2\left<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\right>NI\left<\begin{matrix}CH_2\\CH_2\end{matrix}\right>CH_2.$$

This salt crystallises from absolute alcohol in colourless plates melting at 174°. These are somewhat hygroscopic, but much less so than the bromide or chloride, both of which were found by Gabriel and Stelzner to be too deliquescent for analysis:

0·2548 gave 0·3520 CO_2 and 0·1490 H_2O. C=37·67; H=6·5.
$C_8H_{16}NI$ requires C=37·80; H=6·32 per cent.

On treatment of this salt with moist silver oxide, the corresponding hydroxide is obtained as a syrup, which on distillation yields an oil boiling at 100°/10 mm.

As described above, this oil is *γ-hydroxypropylpiperidine*, $C_5H_{10}N·CH_2·CH_2·CH_2·OH$, which may also be prepared by the action of trimethylenechlorohydrin on piperidine, and treatment of the product with potassium hydroxide. It has a strongly alkaline reaction, and an odour like that of piperidine. It is somewhat miscible with water, and boils at 211°. It has D_0^{16} 0·89427, and $n_D^{16·8}$ 1·45094. With benzyl iodide it gives *γ-hydroxypropylpiperidine benzyl iodide*, $C_5H_{10}NI(CH_2Ph)·CH_2·CH_2·CH_2·OH$, which crystallises from alcohol in slender, colourless prisms, melting at 162°:

0·1710 gave 0·3115 CO_2 and 0·1035 H_2O. C=49·6; H=6·7.
$C_{15}H_{24}NI$ requires C=49·8; H=6·68 per cent.

γ-Hydroxypropylpiperidine, when treated by the Schotten-Baumann process with benzoyl chloride, yields *benzoyloxypropylpiperidine*, $C_5H_{10}N·CH_2·CH_2·CH_2·OBz$, which is an oil having an alkaline reaction and readily soluble in alcohol or ether. By passing hydrogen chloride into a solution of this ester in ether, the *hydrochloride*, $C_5H_{10}N·[CH_2]_3·OBz,HCl$, is obtained, which crystallises from alcohol in colourless prisms melting at 186°:

0·2556 gave 0·1280 AgCl. Cl=12·4.
$C_{15}H_{22}O_2NCl$ requires Cl=12·52 per cent.

II.

The method adopted for the preparation of β-chloroethylpiperidine and the corresponding iodoethylpiperidine was generally the same as that employed by Marckwald and Frobenius (*loc. cit.*), but it was found that the compounds could be obtained in a state of greater purity by heating β-hydroxyethylpiperidine with concentrated hydrochloric acid at 150° or with fuming hydriodic acid at 100° for eight hours.

β-Chloroethylpiperidine hydrochloride prepared in this way was found to melt at 231° (Marckwald and Frobenius gave 208°).

β-Iodoethylpiperidine hydriodide crystallises from alcohol in colourless prisms melting at 212°:

0·2110 gave 0·1760 CO_2 and 0·0785 H_2O. C=22·7; H=4·1.
$C_7H_{15}NI_2$ requires C=22·8; H=4·05 per cent.

Diethylenedipiperidine di-iodide was described by Aschan (*loc. cit.*), who gave the melting point as 295°. When prepared by the action of heat on iodoethylpiperidine, it is obtained in a pure state and melts at 330°.

Ethylenedipiperidine dibenzyl iodide was found to be a convenient substance for the recognition of small quantities of ethylenedipiperidine. It is formed by warming ethylenedipiperidine with benzyl iodide, and is very sparingly soluble in alcohol, from which it separates in small prisms melting at 205—206°:

0·3147 gave 0·2230 AgI. I=38·3.

$C_{29}H_{42}N_2I_2$ requires I=38·48 per cent.

In conclusion, the author desires to record the great loss which he has suffered in the tragic death of the late Dr. H. O. Jones, F.R.S., and to acknowledge how much assistance and encouragement he received during this work from the late Fellow, whose fate is so deeply mourned by all chemists.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CCXIV.—*The Alkaline Condensations of Nitrohydrazo-compounds. Part II.*

By ARTHUR GEORGE GREEN and FREDERICK MAURICE ROWE.

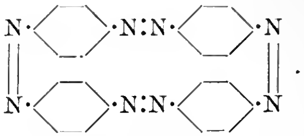
IN a former paper on this subject (Trans., 1911, **99**, 1960) Green and Bearder have studied the transformations effected by alkalis on 4:4′-dinitrohydrazobenzene, and have pointed out the analogy which these reactions present to those occurring in the stilbene series. The first product of the reaction is an unstable nitroso-derivative, which by further condensation is converted into bisnitrobenzeneazo-azobenzene (dinitrotrisazobenzene),

$$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2,$$

the nitrogen analogue of stilbene-yellow. The same substance has since been obtained by Witt and Kopetschni (*Ber.*, 1912, **45**, 1147) by heating 4:4′-dinitrohydrazobenzene with absolute alcohol at 170°.

In order further to establish the analogy indicated, we have submitted this compound to alkaline reduction. The product obtained was tetrakisazobenzene, a deep red substance which, like its analogue, Mikado-orange, dissolves in concentrated sulphuric acid with a pure blue colour. There is formed simultaneously, especially when an excess of reducing agent is employed, a certain quantity of bisaminobenzeneazo-azobenzene (diaminotrisazobenzene), $NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2$, described by Witt and Kopetschni (*loc. cit.*).

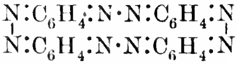
Tetrakisazobenzene,



The reduction is best effected by means of alkaline phenylhydrazine, employing the dinitro-compound in a finely divided state, such as is obtained by dissolving it in concentrated sulphuric acid, pouring into iced water, and washing free from acid. The paste thus obtained from 1 gram of the dinitro-compound is mixed with 40 c.c. of aqueous sodium hydroxide (40 per cent. NaOH), and a solution containing 0·9 gram of phenylhydrazine is added in the cold. The mixture is first gently warmed, and finally boiled until the precipitate is of a dark red colour. The course of the reaction may be readily followed by dissolving small samples of the product in concentrated sulphuric acid, when a blue colour indicates complete reduction. After dilution with water the precipitate is collected and extracted moist with cold pyridine, which dissolves the bisaminobenzeneazo-azobenzene formed simultaneously. The residue is washed with ether and dried. It forms a dark red, granular powder, sparingly soluble in all solvents. In concentrated sulphuric acid it dissolves with a pure blue colour. Attempts to sulphonate the compound with fuming sulphuric acid in order to investigate its dyeing properties did not succeed:

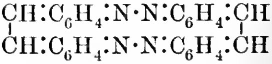
0·0865 gave 0·2175 CO_2 and 0·0324 H_2O. C=68·57; H=4·16.
0·1212 „ 0·3062 CO_2 „ 0·0440 H_2O. C=68·90; H=4·06.
0·1541 „ 34·8 c.c. N_2 at 19° and 763 mm. N=26·14.
$C_{24}H_{16}N_8$ requires C=69·23; H=3·84; N=26·9 per cent.

In the blue sulphuric acid solutions of this compound and of Mikado-orange, the presence of salts of quinonoid bases of the type



$$\begin{array}{l} N{:}C_6H_4{:}N{\cdot}N{:}C_6H_4{:}N \\ \vert \qquad\qquad\qquad\qquad\quad \vert \\ N{:}C_6H_4{:}N{\cdot}N{:}C_6H_4{:}N \end{array}$$

and



$$\begin{array}{l} CH{:}C_6H_4{:}N{\cdot}N{:}C_6H_4{:}CH \\ \vert \qquad\qquad\qquad\qquad\qquad \vert \\ CH{:}C_6H_4{:}N{\cdot}N{:}C_6H_4{:}CH \end{array}$$

may be postulated.

Bisaminobenzeneazo-azobenzene was obtained from the pyridine extract and recrystallised from xylene. It forms garnet-red crystals melting at 294°. It is soluble in alcoholic hydrochloric acid with an orange-red colour, and dissolves in concentrated sulphuric acid with a violet-red colour, becoming greenish-blue on dilution with water.

DEPARTMENT OF TINCTORIAL CHEMISTRY,
THE UNIVERSITY, LEEDS.

BECQUEREL MEMORIAL LECTURE.

DELIVERED ON OCTOBER 17TH, 1912.

By SIR OLIVER LODGE, D.Sc., LL.D., F.R.S.

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The Discovery of Radioactivity, and its Influence on the Course of Physical Science.

PART I.—GENERAL.

THE atmosphere of physical science at the present time is rather a strange one. It is characterised by a large amount of speculative activity, on the one hand, and by an exceptional amount of fundamental scepticism on the other. The two attitudes in fact coexist, may coexist in the same individual, and one may be a consequence of the other. For much of the speculation is sceptical in origin, and much of the scepticism is speculative.

There was a time, within easy memory, when the progress of discovery was placid and peaceful. It seemed to proceed along well-worn channels, and to be based upon the most thoroughly substantial knowledge of the past. The great Victorian era in physics was a development of Newtonian mechanics; and the foundation-stones of science seemed well and truly laid.

Philosophers and biologists attended to their own fields of work, and so for the most part did mathematicians and chemists; each group proceeding on its own lines without much regard for the others. Now, all is changed:—

Chemistry has borrowed the idea of evolution from biology, and is trying to extend it from the origin of species to the origin of atoms; though some chemists reject all this as baseless speculation, and pour modulated scorn upon the few recent discoveries which physicists are willing to accept.

Biologists have been ultra-speculative in their quest for the origin of life, and are turning their attention to metaphysics and philosophy, some of them in an energetic and pugnacious manner.

Mathematicians disport themselves destructively among what have seemed the realities, the very data, of physics; distributing an atmosphere of doubt and hesitation almost equally over space, time, matter, and motion, and treating the ether with a veiled contempt. Philosophers question the correctness of our most fundamental laws—doubting, for instance, even the conservation of energy, and readily assimilating the sceptical utterances of those whom I have for the nonce described as mathematicians, though it is but an active group or school of mathematicians who take this line.

And physicists, or some of them, are seeking to dispense with Newton's laws of motion, to supersede that dynamical basis on which they have built for so long, to regard all laws as merely conveniences of expression, and are trying if they can manage to sustain their science on a basis of action at a distance, fluid electricity, corpuscular light, and caloric heat.

General Effect of New Discoveries.

Bethinking oneself of a cause for all this, it appears that, whenever a discovery of striking novelty has been made, there is a tendency to consider that it not only supplements, but also supersedes and even negatives, a great many of the opinions which were held before; and hence an epoch of discovery is often followed by an era of scepticism.

Discoveries are of two chief kinds—the discovery of law and the discovery of fact. The two tend to become inextricably interwoven: the discovery of law often leads to the discovery of new facts, and the discovery of new facts to either the formulation of new laws or new modes of statement, or to the resuscitation of discarded ones.

As examples of the discovery of *law*, I instance Newton's gravitational theory of astronomy, and Maxwell's electromagnetic theory of light. Discoveries of this kind take their place among the most prodigious efforts of the human intellect.

Smaller in achievement, but great as generalisations, I naturally mention also the atomic theory of chemistry and the conservation of energy.

As examples of the discovery of *fact*, I might instance the prehistoric discovery of flame, the discovery of static electrification, of the electric current, and of magneto-electricity; and with these I would place the discovery of the electron, and the discovery of spontaneous radioactivity.

Of all the facts discovered during the last half century, I suppose that Röntgen's X-rays excited the most popular astonishment; and certainly they were sufficiently new. Nevertheless, existing theory had a place for them, as soon as the electronic notion of cathode rays was admitted—at least, on the assumption that they are pulses in the ether, a view held by most people, and still to be regarded as orthodox. For their immunity from refraction was provided for in Helmholtz's singularly comprehensive "Theory of Dispersion," their penetrative quality was a natural consequence of the thinness of the pulse shell; whilst their origin, as due to the sudden stoppage of a minute electric charge, was not only accounted for, but actually necessitated, by the radiation theory of Larmor.

Hence, if called upon to compare the discovery of Röntgen with the discovery of Becquerel, I should give the palm of novelty to the latter; for the spontaneous splitting up of atoms, and the consequent expulsion of constituent fragments, was not provided for on any theory. It was a revolutionary new fact; although it is true that this view of it was not immediately recognised as an explanation, and although certainly Larmor's electronic theory of radiation, combined with Zeeman's experimental discovery, made some of us very willing to recognise the truth of the disintegration hypothesis as soon as it was promulgated on a basis of fact. Meanwhile, and quite independently of any explanation, the bare fact of radioactivity, with a convenient means of detecting and measuring it, was quickly followed by the brilliant and exciting discovery by Madame Curie of a substance which exhibited the power to an extraordinary degree.

A discovery of real and essential novelty can never be made by following up a train of prediction. It is often made during the process of following a clue, but the clue does not logically lead to it. A really new fact comes always as a side-issue—something unexpected and something that might easily have been overlooked. In so far as it fails to have these characteristics, it cannot be essentially, and in the completest sense, new. The discovery which has been pointed to by theory is always one of profound interest and importance, but it is usually the close and crown of a long and fruitful period; whereas the discovery which comes as a puzzle and a surprise usually marks a fresh epoch and opens a new chapter in science.

Discovery of Radioactivity.

So it is with the discovery of spontaneous radioactivity. The thing that was being looked for by Monsieur Henri Becquerel was the possible emission of Röntgen rays by a substance in a state of fluorescence. It was a reasonable thing to look for, although no theory exactly pointed in this direction; and had it been found it would have been an interesting extension of our knowledge; but the kind of radiation actually detected turned out, when critically examined, to be for the most part not Röntgen rays at all, but corpuscular, and to have nothing to do with fluorescence.

Stimulated by his father's researches in the fluorescence of minerals, and by the possession of many fine specimens, among others a beautifully fluorescent salt—the double sulphate of uranium and potassium—which had been made by him for his father many years ago, Henri Becquerel set himself carefully and critically to examine the kind of penetrating radiation which fluorescent substances exposed to light might possibly be found to emit, such as was also in a preliminary way detected by Niewenglowski, and later confirmed by Troost. What he sought he did not find, but by deserved good fortune he had the happiness to find something much more important, thus writing his name large in the history of Chemistry and Physics for all time.

The process of discovery is well known, but may be briefly recapitulated. This will, however, be most conveniently done later on, when giving a general outline of his life work.

Such a discovery is quite easy to miss. The late F. Jervis Smith, of Oxford, told me that he missed the discovery of Röntgen rays by a trifle; and other experimenters with Crookes's tubes must have missed it too; for whenever the vacuum in such a tube rises considerably, X-rays are likely to be emitted, and to take effect, whether perceived or not, on anything susceptible in their neighbourhood. Jervis Smith, in fact, noticed that boxes of photographic plates which he needed for his work were liable to be fogged if allowed to remain in the neighbourhood of active Crookes's tubes. Presumably he thought the cause to be some merely chemical effluvium, such as ozone or oxides of nitrogen getting into the box, or perhaps he did not speculate on the cause at all, but merely regarded it as a nuisance, interfering with the steady course of his work. Anyhow, he seems to have instructed the laboratory attendant to keep the boxes in a cupboard well away from the fogging influence—a most natural thing to do, and one with which every experimenter must sympathise.

Röntgen, however, as is well known, instead of a box of photographic plates, happened to have a surface coated with fluorescent salt near his vacuum tubes, and although screened from the light its shine caught his eye in a more attractive and attention-compelling manner.

In Becquerel's case the phenomenon looked for appeared to exist, in the way expected, although it was feeble and needed long exposure; but repetition in different circumstances showed that the agent which was expected to produce the effect, namely, fluorescence under the action of light, was inoperative: the action turned out to be spontaneous, and to be dependent only on the kind of mineral used. So much so that no method of hastening or stimulating—nor, indeed, of retarding—this kind of radioactivity, beyond judicious selection of substance, is known to this day.

The following statement concerning the discovery is made by Professor the Hon. R. J. Strutt:

> "It occurred to Professor Henri Becquerel, of Paris, to try whether these salts, when luminescent under the influence of light, would give out Röntgen rays. He exposed a photographic plate, wrapped in black paper, to the action of the luminescent salts, and found, after an exposure of some days, that a distinct impression had been produced on the plate,

which appeared on development. It was natural to conclude that Röntgen rays were given off, as had been thought likely.

"Extraordinary as it may seem in face of the result, this conclusion, as well as the reasoning which led to it, was quite mistaken. We now know that the fluorescence of the glass has nothing to do with the production of Röntgen rays. We know, further, that the fluorescence of uranium salts is quite unconnected with the invisible rays which they emit. And lastly, we know that these latter are of a quite different nature from the Röntgen rays! It seems an extraordinary coincidence that so wonderful a discovery should result from the following up of a series of false clues. For we can obtain the Röntgen rays even better by letting the cathode rays fall on a metal surface which is not fluorescent instead of a glass one which is. We can obtain invisible radiation, able to penetrate opaque substances, from uranium in the metallic form, which is not fluorescent. And lastly, as we shall see in the sequel, these uranium rays differ altogether in their nature from the Röntgen rays."

All this does not detract from the merit of the discovery; it rather enhances its practical importance, for, as we have already said, it is a feature inevitable when the facts to be discovered are really and essentially new.

Rapid Survey of Immediate Developments.

Discovery of the nearly non-deflectable and readily absorbable, or α, rays was made by Professor Curie by the electrical method. The most important examination of their properties was made by Professor Rutherford. His results were confirmed by M. Becquerel, who likewise examined the α-rays emitted by polonium, where they are unaccompanied by rays of the β- and γ-varieties, and showed that their magnetic deviation increased at a distance from the source.

An early photographic study of β-rays, and of their magnetic deflexion, was made with fair completeness by Becquerel himself. One of his experiments, exhibiting the deflexion in a striking way, consists in placing a little radium salt in a lead vessel on the back of a photographic plate—which is thus screened from any direct action—and then deflecting the rays, by means of a magnet, right round on to the under surface of the plate, whereon shadows of interposed objects can be thrown in curious fashion by these circularly-travelling rays.

The non-deflectable but very penetrating variety, the so-called γ-rays, were discovered by Villard, whose results were soon confirmed by Becquerel.

The discovery of the new element radium followed on a purely quantitative investigation as to the radioactivity of different materials carried out with exemplary pertinacity and genius by Madame Curie; just as the other rather sensational and admirable discovery of argon resulted from a quantitative investigation by Lord Rayleigh into the varieties of nitrogen apparently obtainable from different sources.

In both these cases the discoverer himself, with a colleague, worked out many of the properties of the new material; in the case of Becquerel this work was from the first conspicuously shared in by others; thus, Sir William Crookes chemically separated off the greater part of the activity of uranium, as what he called uranium-X, and by systematic treatment, renewed after the lapse of a year, detected the prime facts of (*a*) the gradual decay in its activity, and (*b*) the renewal of the activity of the original stock to a compensating extent: thus beginning to open the eyes of physicists to what was really happening, and paving the way for the brilliant and extensive series of experiments by Professor Rutherford and his associates.

The history of all this is so recent, the facts are so numerous and so fairly well known, they are related in so many accessible books, and they are of so great bulk and variety, that it would be impossible usefully now even to touch upon them or to attempt to follow the historical course of development any further. Suffice it to say that Rutherford measured the atomic weight of the α-particles by applying a magnetic field to their trajectory, and thereby showed that they were corpuscular, not in the electronic sense but in a sense definitely material, being probably either a molecule of hydrogen carrying the electrolytic unit of positive charge, or else an atom of helium with a double unit of charge; and he also displayed a gas-like emanation of high atomic weight, great activity, and short life; on the strength of all of which he, together with Soddy, started the idea of atomic disintegration, not as a speculation, but as an actually observed fact. Later Ramsay and Soddy by spectrum analysis definitely established helium as one of the products of disintegration of this radium emanation, which itself appears to have a characteristic spectrum and is regarded as a short-lived element.

In addition to the atomic bombardment or α-particle projection, electrons are thrown off as if from a cathode, although with exceptional velocity, as β-rays; and γ-rays are likewise ejected, apparently akin to those of Röntgen, although with exceptional penetrating power. All these exert an ionising action on the substances through which they travel, into the consequences of which a great many observations have been made by Professors Barkla, Townsend, and others; and there appear to be other rays, probably electrons travelling at too slow a rate to ionise effectively and perhaps associated with emission of α-particles, which have been called δ-rays.

But their slowness is relative, for it is about 3×10^8 c.g.s. or 2000 miles a second.

All these forms of activity are of profound interest, but their importance is overshadowed by the less purely physical, and more directly chemical, phenomena—namely, the emanation, the α-rays, and the other products of disintegration; for thus is demonstrated, for the first time in the history of science, the conversion of one substance into another, the gradual breaking up of an atom by some kind of successive explosions or disruptions, and the consequent generation of one substance after another; among which radium and its emanation, and possibly lead, occur successively at the heavy or gun end, whilst helium and probably hydrogen are found at the light or shot end of the explosion.

(Taking this as the origin of all the lead there is—that is, assuming that it has all descended either from uranium or from some heavy atomed substance of which uranium is the best known surviving representative and a stage through which the process must have passed—radium being another stage, but too short-lived to be usefully considered in the present connexion—a little arithmetical calculation concerning the age of the earth, in this sense, can be made, thus:

Let U_0 represent the original amount of uranium at the beginning; and let it decay at rate k, so that after a time, t, the residue in existence is

$$U = U_0 e^{-kt}.$$

Let lead represent the final result of the decay, itself being considered comparatively permanent, so that the amount of lead now existing is

$$Pb = U_0 - U.$$

Finally, let the amount of lead existing at the present time be n times the amount of uranium now existing, so that

$$Pb = nU;$$

it will follow, by combining these three equations, that the time elapsed since the beginning of the planet in this sense is

$$t = \frac{1}{k} \log_e (n + 1).$$

Now Professor Rutherford's estimate of the numerical value of the logarithmic decrement of uranium is 10^{-9} per annum; hence $1/k$ equals a thousand million years.

What estimate to make for n, the ratio of the extant lead to the extant uranium at the present time, I have no idea; but the datum only enters into the result under a logarithm, and therefore does not affect its magnitude very conspicuously. If we guess, from the relative prices, that $n = 20$, the calculated age is 3000 million years;

whilst if we make a much larger estimate and suppose n to be 200, the 3000 only increases to 5000; and, inversely, if n is only 2, the age is still 700 million years.)

It is needless to emphasise the extraordinary suggestiveness which the instability and intense energy of atomic structure, thus demonstrated, confers upon our ideas of material atoms in general, since it is surely probable that the stability of the atom of the better known elements, especially of the heavy ones like lead, mercury, and gold, is, after all, only a question of degree. Some substances last a few minutes, others a few weeks or years, some centuries, and others millions of æons—these last being naturally more plentiful, like a population with a low death-rate—yet it must surely be considered unlikely that any such atomic groupings are so devoid of internal energy as to be endowed with an absolutely permanent structure incapable of further subdivision.

(Incidentally, I would heartily deprecate any squeamishness about applying the historic term "atom" to elementary units, able to give a definite spectrum and to form chemical compounds of customary character, merely because the progress of discovery has rendered the derivation of the word inappropriate.)

Intrusion of Scepticism.

So far, it has all seemed plain sailing; but now has come the era of scepticism, and an attempt to limit science to purely material entities and to reduce Physics to a sort of glorified Chemistry, to return, in fact, to the kind of ideas which prevailed in the golden age of Chemistry, near the early part of last century, and to discard everything relating to an ether of space.

For instance, as to the nature of the γ-rays, Professor Bragg, late of Adelaide, now of Leeds, has raised an interesting controversy; and has adduced experiments of his own in support of his view that they, as also their congeners the X-rays, are not ether pulses at all, but are corpuscular; being neutral molecules, consisting, it may be, of positive and negative electricity in combination, ejected in a singularly penetrating manner; ejected possibly, not with exceptionally high velocity, but with their electric field so shut up in the molecular interior as to have no links with the outside world, and therefore to be able to travel far through crowds of other molecules without ionising them, and so without being stopped by the exhaustion of energy required for the ionising process. So long as the oppositely charged hypothetical constituents are combined, they have little chemical influence; but Professor Bragg supposes γ-rays to be broken up after a certain length of adventurous journey, and thus, by dissociation, to give rise to β-rays, and I suppose to some kind of positive rays also. Certainly γ-rays, as they are absorbed, do give rise to β-rays; but this is also a natural consequence of their nature on the orthodox or ether-pulse theory; for just as pulses are generated by means of suddenly stopped electrons, so, in the act of starting other electrons, the pulses may be destroyed.

Professor Bragg's arguments as to their corpuscular nature are based on the secondary effects of γ-radiation, and on the unsymmetrical character of the resulting β-ray distribution before and behind a pair of absorbing plates of different obstructive powers. The arguments are set forth in a properly substantiated manner by their author, and are not to be treated cavalierly. They appear to have secured the adhesion of Professor Callendar, who, in his Presidential Address to Section A at Dundee this year, expressed approbation of Professor Bragg's view; but for myself I feel unable to entertain the idea seriously, not only because, so far as I can follow the argument, it appears far from crucial, but because the ether pulses of the orthodox view are so clearly indicated and indeed necessitated by theory. This is markedly true in the case of *X*-rays, which are known to arise at the sudden stopping place of rapidly flying electrons; and *X*-rays are not supposed by anyone to differ greatly from γ-rays.

Larmor's radiation-theory makes the rate of loss of energy of any accelerated electric charge e quite definite, and equal to $\frac{2\mu e^2}{3v}(\mathrm{acc})^2$, where v is the velocity of light.

This furnishes in my judgment a quite fundamental point of view. Ethereal radiation is certainly due to the acceleration of electrons—proportional, in fact, to the square of the acceleration. So when an electron is suddenly stopped or started, an ether pulse is inevitable. In the case of stoppage we call the pulse an *X*-ray; in the case of starting we call it a γ-ray. And the properties of the thin shell of radiation, which *must* then be started, agree with the known properties of *X*- and γ-rays, which all admit to be alike.

This statement Professor Bragg and those who adopt his opinion will somewhere disagree with, for reasons given; although in what way precisely they meet the theoretical objection, manifestly—or at least superficially—opposed to the conclusion which they draw from the experiments, I do not yet know, although I can make a surmise from some considerations which follow.

Certainly quickly-flying electrons are stopped at the target of a cathode-ray tube; and certainly electrons are started, with still higher velocity, and more suddenly, at a source of radioactivity of the kind which emits electrons—such as radium-*C*. When only α-rays are emitted, γ-rays are not found, or are not plentiful; but they invariably accompany β-radiation; and the reason for this is manifest in the light of an ether theory of radiation.

The question therefore arises as to what ethereal radiation is really like. In so far as Professor Callendar intends to advocate a dual constitution for the whole ether of space, making it consist essentially of interlocked positive and negative electricity—which whatever it really means must at least denote two constituents of exactly opposite properties which are constantly being sheared, that is, strained in opposite directions (compare "Modern Views of Electricity")—I am in sympathy with the attempt, for I have long felt that the progress of discovery would lead us somewhere in that direction, although a great deal more definiteness must be introduced before it is anything but a guess and an anticipation. On this view, however, it becomes just possible to conceive of an isolated unit of ether travelling among the rest, like a minute ejected double corpuscle, a combined plus and minus unit of charge, of the order of electronic size without associated matter; not so much an ether pulse as a minute ether projectile. The idea is not unreasonable, but at present I am unable to agree, without further evidence, that it represents the probable nature of γ- and X-rays.

There are those, however, who hold that even light, which for a century has certainly seemed to consist of ethereal waves or pulses, is likewise corpuscular; and that if it is not wholly explicable in terms of particles shot off from bodies, such ejected particles must form the beginning and substratum of an explanation, with something periodic superposed upon the projectiles, after the manner of Newton.

It is not surprising that an attempt should be made to revive in some form the corpuscular theory of light, even if light be now regarded as an electric manifestation; for electricity, too, has become corpuscular, and the flow of electricity through metals is now regarded as a streaming of actual bodies—detached, or so nearly detached as to be readily interchangeable, from the fixed atoms of a solid, and therefore migratory—flowing from one metal to another across a junction as a fundamental kind of material thing which is able to exist in association with every kind of matter. Its association is loose enough in metals, which are therefore good conductors; whereas in another class of substances the corpuscles are so tightly held in combination with individual atoms that they cease to be migratory, and the substance is an insulator, that is, one which can only transmit a current by violence and disruption.

The migratory and ionic theory of *liquid* conduction, and of the constitution of electrolytes generally, entered the field first, and, although stoutly resisted by some chemists, appears to be holding its own, and to be invading one province of physical chemistry after another with marked success.

Materialising Tendency in Physics.

The ionisation doctrine and its many developments may be regarded as an encroachment of physics on the preserves of chemistry, since it has certainly modified ideas about the nature of solution; but there is a converse process now going on, and in the course of a sort of triumphant materialisation of obscure entities, achieved at any rate hypothetically and speculatively if not yet in any substantial manner, Chemistry seems to be dominating emancipated parts of Physics.

The latest and most astonishing attempt towards the reconversion of Physics into Chemistry appears in a brilliantly clever and apparently serious Address to Section A by Professor Callendar, this year, on the resuscitation of caloric or the material theory of heat—a theory which carries with it the ancient view that physical changes of state, such as vaporisation and liquefaction, are really the solution of matter in the substance of that apparently imponderable material caloric, and vice versa.

After this it is barely surprising to hear the biologists call upon the chemist to explain the phenomenon of life, and to produce in their glass vessels—if only they can stumble on the right environment, and on a judiciously combined assortment of material—some low form of living matter.

In view of the remarkable experiments recently made on the influence of various strengths of mere salt solutions in fertilisation and cross-breeding, it is not surprising that an anticipation of the kind should be promulgated. At present it is no more than a speculation, but if followed up, although it may not lead to the result anticipated, it may lead to others of perhaps equal interest.

The careful and accurate and painstaking and recording experimenter is always justified, and sometimes he is rewarded by results; but experiments of this kind, conducted in the dark as it were—that is, without a clue of theory—conspicuously need the utmost care; and concerning such experiments considerable scepticism is for a time legitimate and necessary. Of such kind, in that respect at least—I may incidentally mention—are some experiments and observations with which I have been more or less associated in connexion with what is known as psychical research. Positive results in this subject, when established, must be of extraordinary importance and novelty, but to establish them excessive care is necessary, and until they are substantially verified respectful scepticism is entirely legitimate.*

Tendency to Return to Ancient Views.

All this tendency to return to discarded hypotheses and revivify old beliefs—for spontaneous generation is, I suppose, a very old belief or superstition—is a matter of great interest; and it is astonishing to find how much can still be said for ancient views. Forty years ago the Caloric theory of heat seemed dead beyond redemption, and I do not say that it yet lives, but the ingenuity of Professor Callendar finds a great deal to say for it, some of it of a cogent kind; it appears to be quite a possible mode of expressing facts, and one that is perhaps convenient for several non-elementary purposes.

At any rate, Professor Callendar's Address to Section A at Dundee confers on the abstract mathematical idea of *entropy* a local habitation and a name which I for one had never previously recognised, and which I fancy neither Rankine nor Clausius recognised either; whilst it emphasises, what was really never doubtful, the extreme brilliancy of Carnot's treatise on the motive power of heat. Moreover, it unifies the treatment of heat engines and electric motors, so far as can reasonably be expected without the opposition of sign familiar in electricity but presumably without meaning in heat. It is true that the production of fresh caloric during any irreversible process raises a difficulty about regarding heat as a substance; but, from Professor Callendar's point of view, the difficulty is by no means insuperable. The source of the substance can perhaps be traced as readily as we at present trace the source of *heat-energy* when that too is freshly generated by the like irreversible processes.

Then again in early days it was customary to jeer at the prevalent popular habit of speaking of electricity as a fluid, and until we knew more about it the practice was certainly to be deprecated; but now, in the light of further knowledge, something very like an improved and more definite fluid theory seems likely to hold the field.

Hitherto, Röntgen radiation has seemed to belong almost wholly

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* When I speak of psychical phenomena as novel, I do not mean that testimony for their reality is limited to recent times—folk-lore legends about them are as old as humanity; the novelty consists in their now trying to make good their position in a scientific age, and in their appearing in a scientific dress. If we succeed in exposing them to rigid scrutiny, it will be another case of materialising the vague, the discredited, and the unseen. But that seems rather the tendency of science at the present day, and is noticeable in many branches, as I will emphasise later.

to Physics, whilst Becquerel radiation belonged largely also to Chemistry, to which science our friend the late Dr. Russell's radiation or emanation has always belonged wholly; but now judgment as to the nature of Röntgen rays may have to be regarded as open to revision.

We have already called attention to the fact that the undoubtedly corpuscular nature of some kinds of radiation, such as cathode rays, α-rays, and β-rays, has inevitably led to an attempt to resuscitate a corpuscular theory of light; and, if the anti-ether speculators who support the Principle of Relativity are to pave their way into anything approaching smoothness, some form of corpuscular light would clearly be necessary.

THE ATTITUDE TO ESTABLISHED LAWS.

General Physical Laws.

Amid this sea of conflicting hypotheses and guesses what should be our attitude? and how far should we condemn those philosophers who in their anxiety to stem the tide of materialistic philosophy (in which enterprise I for one am a sympathiser) have tried to throw doubt upon certain well-established and fundamental laws of physics—an enterprise wherein, as in duty bound, I part company with them.

I urge that our attitude should be this:

Let us admit that any law applicable to concrete objects (not merely to abstractions), and established by induction on a basis of experience, must necessarily be of the nature of a postulate; but let us hold some of the postulates as so well established and secure that any argument that would necessitate their overhauling is *ipso facto* to that extent discredited, and not to be countenanced unless supported by new and revolutionary facts; and even these new facts we must try to explain in harmony with all well-established laws, rather than as disturbing or negativing them.

In other words, let us seek to reconcile all new facts with the fundamental laws of physics, applied in a proper manner, until compelled to cast about for some higher generalisation. For in all probability that higher generalisation, when it comes, will be supplementary rather than superseding; and the conditions which necessitate its admission will be specifiable and definite when the subject is properly understood.

Among such well-established laws I should place first Newton's laws of motion; remarking that they apply to matter only, not necessarily to ether; and remarking also that effective *mass* may be variable under certain conditions,—as it often is, for instance, simply enough, in the case of a falling raindrop, or of a sphere entering a perfect fluid.

Measurements of e/m, made on particles flying at two-thirds of the velocity of light, are by some said to invalidate Newton's second law. It is to my mind unquestionably preferable to express the fact in terms of variable inertia—the value of the inertia becoming in that case a known function of speed through ether.

Those who disbelieve in ether cannot, of course, agree with this dictum.

Again, the recently discovered *pressure of light* is sometimes said to invalidate Newton's third law. I should prefer to express the fact by saying that, when applying the law quite generally, an ethereal wave-front must be taken into account, as well as matter; and that we thereby get our first mechanical touch with the ether of space.

Supporters of the Principle of Relativity will consider this nonsense.

Another law I should place high and dry out of the reach of immediate controversy, is the Conservation of Energy.

In so far as the actions of living beings seem to conflict with this law, in so far as the facts of guidance and control appear to militate against it (as I for one hold that they do not), I would rather look for some new form of energy, or some ethereal seat of force or reaction, rather than doubt the generality of a comprehensive law of that kind. That law I should assume true; provided always that every form of energy, known and unknown, is taken into account.

Again, the conservation of matter, although it is a law that requires caution in its statement, and although the disintegration of material atoms is sometimes said to upset it, is probably true in essence. We must admit that our category of the thing conserved may have to be enlarged, so as to include electrons and other ethereal groupings or peculiarities, but it seems to me distinctly best to adhere to the idea of the conservation of fundamental substance until irrefragable evidence to the contrary is adduced.

All these laws may some day have to be revised, and at any time they may have to be more carefully formulated; but it is a mistake to be willing too easily to pluck them up and discard them. So it was once with the law of gravitation. Every new perturbation detected in astronomy was liable to raise doubts about the exactness of the index 2 in the statement of the law of inverse square. I do not say that such doubts were illegitimate, although they have proved unnecessary, but I do say that this mode of explanation should be only seriously contemplated when other resources had failed; and as far as I know, other resources have not yet finally failed in any single case.

Among other postulates of high authority I should be inclined to place a wave theory of light—interpreted, of course, in terms of electricity and magnetism, not an elastic solid theory but definitely in terms of ether. For it seems to me that to try to discard the ether on the basis of a Michelson-Morley experiment, which after all is thoroughly and well explained by the FitzGerald-Lorentz hypothesis, is both retrograde and injudicious.

Relativity.

Some mathematicians, among them the late Professor Poincaré, are willing to give away their kindred subject of physics by admitting or maintaining that our laws are not important statements of fact, but are only conveniences of expression. And many philosophers seem eager to accept this vicarious generosity at their hands.

But such repudiation of our claims, and reduction of our life work to insignificance, I altogether deprecate. If we are not seeking real truth, if we are only seeking convenience of expression, the science of physics is not the noble structure which I for one think it.

To take the simplest and most rudimentary example:

Are we to suppose that it is only a matter of convenience whether we say that the earth turns on its axis, or that the host of heaven revolves round it once a day? I hold that the one is a genuine and absolute truth, whilst the other is a genuine and absolute falsehood; and that convenience of expression has nothing whatever to do with the matter, except that the truth must always be ultimately more convenient than error; just as I say that it is true that a train is travelling over the surface of the country, and not true that the ploughed fields and hedgerows are contorting themselves in the eyes of stationary travellers. The relativity of motion, thus pressed, and taking matter alone into account, is really absurd. Yet those who discard the ether are constrained to assert that there is no pragmatic difference between the two forms of statement, and no mode of ascertaining which is true: no meaning, in fact, in absolute motion at all.

On the other hand, those who accept the ether attach a definite meaning to motion through it, and are ready to admit as probable that in ordinary circumstances motion as great as the velocity of light can only be asymptotically reached; or at least that if it is reached or exceeded the first law of motion will, so to speak, break down, that is, become inapplicable, because to maintain the motion a propelling force will be required. Indeed, some day these physicists with whom I agree expect to be able to measure the actual velocity of masses of matter through the ether of space by some definite phenomenon due to *this* kind of relative motion—which is not the kind contemplated by the Principle of Relativity. That principle would lead us to maintain that inasmuch as this kind of motion is meaningless it certainly can never be experimentally proved.

The great thing to avoid in science is negations. Let us make and substantiate positive assertions. But negative assertions—statements as to what does not happen, or what is not possible—although occasionally necessary, are always dangerous, and should be kept in rigorous check.

Life and Radioactivity.

Take, for instance, the attempts to construct living matter out of artificially combined materials. It may be impossible, but the attempt is quite legitimate, and no one can positively say that it will never be successful.

In so far as life demands energy for its peculiar manifestations and trigger-pullings, an available source of such energy can easily be suggested. It may or may not be a useful, that is, a true, suggestion, but the phenomenon of *radioactivity* indicates a possibility. We know now that atoms possess a store of energy which they give off in random directions as they periodically and spontaneously disintegrate. We have also long known, or supposed, that organic compounds left to themselves, apart from the cohering or integrating influences of life, likewise disintegrate and evolve energy—gradually passing down a series of stages, giving off emanations and heat, and ultimately becoming inorganic. A decaying heap of refuse, a pile of manure, represents to me a sort of chemical analogy to the physical activity of uranium.

The one is an affair of atoms, the other of molecules; but in order to be conspicuously radioactive the atom must be large and massive, whilst in order to exhibit organic instability to a high degree, the molecule must be large and complex.

In both cases there appears to be a complex grouping which, either with or without stimulus, disintegrates into something simpler, and generates heat or evolves energy in the process.

Here, then, is a stock of energy running to waste: it would seem eligible for guidance. What life has to do is to control this spontaneous disintegration of protoplasmic cells, to regulate the activity of the ganglia in the brain, for instance, or to suspend the disintegration of organic material until some appointed time, and then to direct it along a determined channel. That is all that a sportsman or artilleryman does with the energy of gunpowder. He withholds its explosion until an appointed time, and then he liberates it in a definite direction. To say that he propels the projectile, and thereby conflicts with the conservation of energy, is absurd. This process of timing and aiming is typical of the control of life throughout. The manner and method by which life achieves this control, it is true, we do not yet know. It is one of the many things which we have to find out. But those who say that life cannot guide material processes unless it is itself a form of energy (which is false, a man is not a form of energy)—those who hold that life cannot, in fact, act at all unless energy is at its disposal (which is certainly true)—forget the apparently spontaneous activity of complex organised molecules, forget the atomic disintegration manifested by radioactivity. Energy is not a guiding or controlling entity at all. It is a thing to be guided. Energy by itself is as blind and blundering as a house on fire or a motor-car without a driver.

There is a great difference, moreover, between matter potentially living and actually alive. It must never be forgotten that in the physical universe our power is limited to the movement of matter: all that happens, after that, is due to the properties of matter and of its ethereal environment. If potentially living matter is ever artificially produced, by placing things in juxtaposition and bringing natural physical resources to bear upon the assemblage—which is all that we can do—then it may become alive. But if this last step is taken, it will be because something beyond matter, and outside the region of physics and chemistry, has stepped in and utilised the material aggregate provided—in the same way, presumably, as that in which it now steps in and utilises the material provided, say, in an egg or a seed. That is my belief, and only in that sense do I anticipate that the artificial incarnation of life will ever be possible. Certainly life has appeared on the earth somehow, and some day it may perhaps appear under observation. In that case it will be said to have been manufactured. It will be manufactured just as much as radium or radioactivity has been manufactured, and no more.

The spontaneous properties of matter, however, are far from exhausted: there may be many yet to be discovered. Twenty years ago no one knew or suspected the property of spontaneous radioactivity accompanied by atomic disintegration. Now it is a recognised commonplace of science.

Tendency to Discard Established Laws.

When radium was discovered many people jumped to the conclusion that the law of conservation of energy had "gone by the board," and that there was not only mystery but "miracle" about the constant evolution of heat by a speck of radium salt. Miracle about it there is none, in any ordinary sense; and the mystery has reduced itself into a consideration of what is the best theory of the way in which electrons and the other atomic ingredients are grouped together, and as to whether their internal energy is due to their static configuration (as Lord Kelvin argued) or to their kinetic orbital movements, as others of us have urged as more explanatory and far more probable.

To suppose the law of conservation upset because a new source of heat is discovered—an unexpected intra-atomic store of energy opened up—is just one of those mistaken attitudes which I deprecate.

In the ether, so I believe, the amount of energy stored is immensely greater than anything which can be housed in a corresponding bulk of matter; and whenever humanity becomes able to tap this ethereal store, our descendants will be liable to go through the same revolutionary perturbation as some of us have gone through; unless they are wise enough to take warning by the past. Whether the ethereal source is being, by any means whatever, unconsciously tapped already, I do not know. There are a few observed facts which to me seem to hint at the possibility of such utilisation: but possibly the store of energy now known to exist inside atoms of matter is more than ample to account for anything of the kind.

Unification v. *Multiplicity of Causes.*

It is reasonable to enter a protest against entertaining the hypothesis of a multiplicity of causes for the same thing, without strong evidence that such multiplicity is necessitated by the facts. In some of the more complex, though it may be ordinary and familiar phenomena, a multiplicity of causes is obvious; for instance, to explain the death of an animal, or the fall of a house, or, again, such things as the settling of dust or of dew, the occurrence of wind, or the variation of terrestrial magnetism, several reasons can be given. But for fundamental things, one cause or one explanation must be expected to overpower and replace all the others, as soon as it is known; for instance, to explain magnetism, or light, or gravitation, or inertia, one explanation of each must surely be fundamental.

To illustrate the matter further: to explain the occurrence of a sound, hundreds of possible causes may be suggested; but to explain sound itself, a definite type of motion of the molecules is all that need be appealed to; and, whatever the kind or the origin of the sound, the same kind of motion, in essentials, is all that we demand. Plenty of variety exists under the main head.

And this commonsense attitude I would adopt in cases where the explanation is not known. Thus, for instance, Larmor has shown that ethereal radiation must be generated by the acceleration of electric charges. If this be granted, as I think it must, the straightforward attitude is to seek to explain *all* radiation of an ethereal kind in that way, and to deny, except on definite evidence, that there is any kind of ethereal wave motion that cannot be traced to electronic acceleration.

Corpuscular radiation, however, undoubtedly exists likewise; and the question of to which category a given radiation belongs is perfectly open.

So also the more general and far more important and difficult question remains an open one whether in some not yet worked-out way a corpuscular radiation can be imagined which has all the essential properties of an ethereal wave or pulse; for in that case we may be able to recognise essential rightness in both points of view, and so be able to unify them—as has so often happened before in the history of science.

Alternative views are not always hostile and mutually destructive, although it sometimes conduces to the progress of science if their supporters think they are; but ultimately it may be found that they represent opposite aspects of a truth as yet imperfectly perceived. Certainly the fact that an advancing wave-front has momentum, exerts pressure, and sustains reaction—has, in fact, many of the properties of matter, except that it cannot rest—is calculated to attract attention and to give pause to anyone inclined to be dogmatic and dictatorial.

Again, J. J. Thomson showed in 1881 that an electric charge possessed the property of inertia, so that when moving it possessed momentum and kinetic energy. It was premature then to pay great attention to this curious and interesting result, which seemed to indicate that *mass* could be reduced to an electromagnetic or ethereal phenomenon; but now that electrons have been discovered, that is, electric charges so concentrated as to exhibit the properties of momentum and kinetic energy to a marked degree—and now that metrical experiments have shown that the electromagnetic part of their inertia is the whole of it, it becomes natural and proper to assume, in default of definite evidence to the contrary, that electromagnetic inertia is the only inertia that exists. That is very far from saying that electromagnetic inertia is thoroughly understood; all that the hypothesis or postulate does is to cause us to look for an underlying meaning for *mass* in ethereal properties, to regard the explanation of inertia as a possible quest for science, and not merely to sit down with folded hands and regard it as one of the fundamental and inexplicable properties of Newtonian matter.

If all mass is reducible to electric charge; if all radiation not of a projectile character is to be attributed to electric acceleration —of which ionic collision or chemical clash is one variety; if all electric currents are electrons or electric charges in motion; if all magnetism is due to the spinning of electrons; if all chemical affinity is really electric attraction over molecular distances—or, what is the same thing, if electrostatic attraction is chemical affinity a long way off—then clear statements of these various facts, when established, would be great generalisations and unifications, such as physicists used to strive for in old days and strenuously look forward to; although in these degenerate days mere convenience of expression is all that appears to be hoped for, and multiplicity of causes, like unexplained action at a distance, seems to be regarded with equanimity.

Meanwhile, I recommend these unified generalisations as postulates, as guides to inquiry, to be held, not dogmatically, but as working hypotheses; the burden of proof being thrown, not so much upon facts which support them—for those are manifestly numerous—as upon facts which render any of them uncertain. Such facts when adduced must be rigorously scrutinised, and not lightly accepted at their face value; still less, of course, must they be rejected as contrary to the laws of nature.

It may seem absurd that any facts could ever be rejected or excluded from contemplation on this latter ground, at this stage of the world's history, and with all the dogmatic errors of the past to guide us; but, nevertheless, I have reason for asserting that it is not so impossible as it ought to be.

MATERIALISING TENDENCY THROUGHOUT SCIENCE.

Discoveries in Biology.

The tendency of present-day science to materialise the invisible or to make concrete and tangible the vague influences previously thought of, has been well emphasised in a paper by Dr. Fraser Harris, of Halifax, Nova Scotia (see a paper called "The Metaphor in Science" in the American magazine called *Science* for August 30th, 1912).

The instances which he adduces are such as the following:

The "acidifying principle," or dephlogisticated air, called by Lavoisier "*the oxygine principle* for those who prefer the same meaning in a Greek dress," is now the familiar oxygen, purchasable at so much per cubic foot, like timber.

So likewise Harvey in 1628 emphasised the probability of some movement in the blood—"movement as it were in a circuit"—*an motionem quandam quasi in circulo haberet.* He had begun to think whether there might not be such a movement, and later on had said "this motion we may be allowed to call circular"; thus the phrase "circulation of the blood" entered into physiology, although the actual fact was not visibly demonstrated until 1660—three years after Harvey's death. Then it became a concrete reality, and is now a common microscopic demonstration in the tissues of a frog's foot.

Again, the "animal spirits," supposed by Willis in 1650 to be driven inwards by the impression of an outside object, so as to give rise to sensation, and then to rebound from within outwards so as to excite movement, are now the constantly experimented-on nerve-impulses, the physical speed of which was measured by Helmholtz in 1850. Furthermore, the energy of even this nerve-impulse is being traced to minute granules or prisms alternately accumulated and consumed in the nerves, called after their German discoverer, *the granules of Nissl.* These appear to be the dynamogenic material widely distributed throughout the nervous system; and "nervous exhaustion," so far from being fanciful, is becoming associated with visible depletion of these microscopic granules.

Then, again, muscular fatigue, understood by most people as merely a particular kind of feeling or sensation, is now made concrete and shown to be the result of mild muscular poisoning, or the deposit of fatigue-toxins in the system.

As for malaria, a term which merely means "bad air," and ague, also vaguely called paludism or the influence of marshes, they are now traced, as everyone knows, to a parasite of the mosquito—traced, that is, to the bite of a thing which can be crushed with the fingers.

Plague or pestilence, also, was in ancient times attributed to various mysterious causes—such as a conjunction of the planets, the taking of a census, or the iniquities of the Jews—but it has now been proved due to a minute vegetable parasite inhabiting the fleas of rats.

The microbe of "influenza," even,—the very name for "influence"—has now been seen by the trained eye of the microscopist; and it is not to be doubted but that further progress in the same direction will be made.

Everywhere, as Fraser Harris well says, indefinite and elusive things have been identified and shown to have a local habitation or a distribution in the recesses of the living body. *The whole tendency has been towards the objectifying of the subjective and the visibility of the unseen.*

It would lead too far away from the subject to speak of the way in which other vague and unseen entities or imaginaries, such as spiritual existences and phantasms, are being brought to book and materialised; nor are the facts yet ripe for public discussion; but in passing I may express my opinion that a materialising tendency is becoming conspicuous here also, and that ordinary mechanical acts and appearances will have to be directly attributed to ordinary or perhaps rather extraordinary mechanical and material causes, whatever their ultimate or indirect meaning may be. In even higher matters, I am convinced that progress lies in the direction of postulating definiteness and of thrusting vagueness out of the field. Skill and instinct are needed, however, to determine when it is time to move, and to discriminate genuine advance towards daylight from benighted blundering into a bog.

Demonstrations in Molecular Theory.

Another thing that has often been considered rather a vague matter of inference, and one on which a good deal of scepticism has persisted for a century, that is, since the time of Dalton—although the hypothesis in one form or another is as old as the Greeks—is the existence of those material discontinuities which are styled atoms. Although the atomic theory of chemistry has held its own, and although chemists have tried to picture to themselves the kind of atomic arrangement or grouping which would account for the observed properties of molecules—among other things for their crystalline interlockings and angular facets—yet chemists have always been careful to say that these pictorial representations were not to be taken literally or supposed to correspond with actual fact, but that they were to be treated in a more or less metaphorical or allegorical manner rather than as statements of reality. Indeed, the tendency was to doubt whether the actual *fact* of such arrangements could ever be perceived; and a good deal of scepticism persisted in the minds of at least a few chemists as to whether "atoms of matter" were more than a convenient verbal expression. It was clearly realised by physicists that atoms and molecules were of so minute a size as to be always beyond direct microscopic vision, since the waves of light, although exceedingly small, are much larger than molecules; and accordingly the eye, however much assisted, could never hope to see such things by aid of the comparatively coarse vibrations of visible light.

But that has not prevented the invention of the ultra-microscope, whereby diffraction phenomena can be ingeniously arranged so as to show, in a sense, the appearance of things far below ordinary possibilities of vision.

Crystal Structure.

And now, quite recently, the announcement is made from Russia that by the use, not of visible or even ultra-violet light, but of ethereal pulses of immensely shorter wave-length—of pulses excited by the sudden stoppage of electrons, and therefore comparable in size rather to electrons than to atoms of matter—by the use, that is to say, of *X*-rays and a photographic plate—it has been possible to examine into and depict the actual molecular arrangement and interior architecture of crystals, whereby the anticipations and geometrical arrangements laboriously arrived at as probable, by the life-work of Mr. William Barlow, F.R.S., and by him in association with Professor Pope, appears likely to be verified, improved, and made definite.

Whatever may be the results achieved so far (and at present detailed information is lacking), the report is too probable to be disbelieved; and however incipient may be the method as at present realised, it can hardly be doubted that on some such lines definite progress will eventually be secured, and the invisible and hypothetical and mysterious once more be brought under actual and definite observation.

I base these anticipations on the diffraction photographs obtained recently by Drs. Knipping and Friedrich, and treated theoretically by Professor Laue; and also upon the testimony of Dr. A. E. H. Tutton, F.R.S., himself an eminent and experienced worker in crystallography. For he has described in a preliminary way discoveries made by Professor von Fedoroff, of St. Petersburg, confirmed apparently in the laboratories of Professors Röntgen and von Groth in Munich, whereby diffraction photographs of what he calls the space-lattice or molecular arrangement in the crystals of zinc blende can be obtained by the use of *X*-rays; the molecules and their actual arrangement in the crystal becoming visible, or inferable, and being such as apparently to confirm the independently discovered and identified types of homogeneous and symmetrical arrangements of the many classes of crystals studied with so much skill and pertinacity by our countrymen above mentioned. This, if it be a fact, will have to be recognised as a striking and admirable case of scientific prediction, the various crystalline structures and accuracy of characteristic facets having been indicated by theory long before there was any hope of actually seeing them; so that once more—always assuming that the heralded discovery is substantiated—the theoretical abstraction will have become concrete and visible.

Brownian Movement.

But, after all, these are static things in comparison with certain discoveries of extraordinary interest developed during very recent years in connexion with the Brownian movement; whereby the kinetic theory of gases has been extended both theoretically and experimentally, and shown to apply, not to molecules only, but also to the spherical particles of a precipitate or liquid emulsion—particles which are perfectly visible in the microscope, and the movements of which can with care be projected on a screen for popular observation. I understand that, quite lately, they have been even kinematographed, by instantaneous photography, at intervals of 1/20th of a second.

These particles have been skilfully shown, by M. Jean Perrin, Professor of Chemical Physics in the University of Paris, to obey gaseous laws in complete detail; and, by measurements made on them, he has not only obtained determinations of the various gaseous constants and atomic magnitudes, but, in the light of the beautiful theory of Einstein, he has furthermore gained ocular evidence of the truth of a great many previously abstract and mathematically formulated laws.

For instance, Maxwell's law of the equipartition of energy—originally applicable to gaseous molecules considered as a system of elastic bodies colliding at perfect random—has been proved to hold in the case of these comparatively great masses, some of them as much as the hundredth of a millimetre in diameter, as well as to the atoms themselves; and certain molecular processes, such as coagulation or the formation of colloids, seem to be becoming visible by their means.

Some of these particles of which the Brownian movement has been observed are truly immense compared with atoms, since particles of ten microns (the hundredth of a millimetre) in diameter are as much bigger than atoms as atoms are bigger than electrons. Their osmotic pressure is less than the thousand-millionth of an atmosphere, but their atomic weight is such that if conceived of as a gas at normal pressure and temperature, and still subject to Avogadro's law, their so-called gram-molecule would amount to 200 thousand tons.

If M. Perrin's contentions are justified, it is, as he virtually says, rather singular to find the number of particles emitted by radium to be connected with Avogadro's constant; and this with the equilibrium distribution of particles in a liquid, and the distribution of energy in the infra-red spectrum, as well as with many other things of extremely diverse character.

Furthermore, these particles can be shown to be disobeying the second law of thermodynamics, at least in a form in which it is often stated; since they rise sometimes in a lighter liquid, and thereby extract work from it, although the temperature is perfectly uniform and the liquid stagnant; thus showing—what indeed is well known—that the liquid is only statistically stagnant, whilst its individual molecules are in a state of strong agitation, and that the uniformity of pressure experienced by every side of a submerged body is only an average effect, true when the surface is sufficiently large for the law of averages to be valid. These particles are too small to satisfy this condition, and accordingly they are bombarded in an unbalanced manner, and move irregularly. But the behaviour of these particles also emphasises the fact, which appears to be less well known than it ought to be, that the second law of thermodynamics is essentially a statistical law, not a fundamental law of nature; it concerns practical methods of using the irregular and unorganised motion called heat. That is to say, the second law is only applicable when the terms *heat* and *temperature* are appropriate; and these terms are necessarily concerned with large groups of molecules, and have no ultimate meaning when individual particles are attended to, for then their heat energy may be conceived of as being as available as any other kind of motion energy, for instance. that of a piston rod or a flywheel.

Maxwell's Demons.

In the case of the Brownian movement the particles watched are small enough to demonstrate the bombarding influence of small groups of particles; and accordingly they behave somewhat as Maxwell's demons behave, except that they are purely inert and unintelligent—taking blows as they find them by chance, not looking for them—and therefore do not exert any demoniacal or discriminating influence the effects of which can be detected on a large scale; they require to be watched individually for any incipiently demoniacal occurrences to be observed.

And, further, it appears that the motion of these particles is so intricate and irregular, so polygonal and revolutionary and discontinuous, that no reasonable tangent can be drawn at any point of their path, so that they have suggested to M. Perrin—no doubt half-jocularly—the physical realisation of those curious curves, invented by mathematicians and hitherto supposed limited to abstract mathematics, which, although essentially continuous, have an infinitude of tangents at every point and no differential coefficient.

I doubt if physicists ever expected to be able to measure, still less actually to see, the effect of a single atom. But the extraordinary energy with which α-particles are ejected from a radioactive substance has now enabled this remarkable step to be taken. The ionising effect of a single particle, admitted through a minute orifice, is measurable by an electroscope; and the flash which it produces, when it strikes a target of sulphide of zinc, is popularly familiar in Crookes's spinthariscope.

The speed of these charged atomic projectiles, thus spontaneously ejected from radium by intra-atomic energy, is such that a milligram of matter travelling with the same speed could do as much damage as a one-and-a-half ton shot fired from a cannon.* So, knowing this, it is not surprising that, although only single atoms, they can make a crystal flash where they strike, or can ionise 86,000 molecules of air; but it remains still surprising to learn from Rutherford's measurements that a milligram of radium is continuously ejecting 34 million of such projectiles every second. Yet these are things about which scepticism is quite inappropriate.

Scientific Consequences of the Discovery of Radioactivity.

The discovery of radioactivity, developed as it has been by the labour of physicists still working in full blast, has resulted in such important consequences as the following:

1. Definite speculation as to structure of the atom.
2. Discovery of an immense quantity of intra-atomic energy.
3. A new kind of chemical change independent of any physical surroundings.
4. Transmutation of one element into others, and an estimate of the life-time of each.
5. A probable source for helium and the other inert gases.
6. The probable parentage of lead, and ultimately of other well-known substances.
7. Detection of the ionising power of rapidly-moving charged particles.
8. Calculation of the energy required to ionise an atom of a gas.
9. "The close connexion of the photographic and phosphorescent actions of the α-rays with their property of producing ions, raises the question whether photographic and phosphorescent actions in general may not, in the first place, be due to a production of ions in the substance."—(Rutherford.)
10. Data required for calculating the age of the earth supplemented so greatly that previous calculations are superseded.
11. Incipient computation of geological eras and dates.

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* At a speed of 1700 feet a second.

12. A possible additional source of solar and stellar energy.

13. Ability to make observations on matter and electric charges moving with nearly the speed of light.

14. An experimental reduction of material inertia to electromagnetic and ethereal influence.

15. A method of gaseous analysis which exhibits not only the kind of substance, but its state of molecular aggregation, and likewise the electric charge which each molecule or group carries.

16. A method of determining atomic weights, even of very evanescent substances.

And the list can be extended.

PART II.—HISTORICAL.

Work of Henri Becquerel.

Henri Becquerel, born in 1852, lived from his infancy in the atmosphere of the laboratory of the National Museum of Natural History in Paris. At the age of nineteen he entered the École Polytechnique. From it he went into the Corps des Ponts et Chaussées, and studied as an engineer for three years. In 1875 he published a work which gained him a position as Demonstrator at the École Polytechnique, where he became Professor in 1895. In 1878, at the death of his grandfather, he became assistant in the Museum, under his father, then Professor; and him also he succeeded in 1892. He was admitted into the Academy of Sciences in 1889, at the age of thirty-six.

He was greatly attracted by Faraday's discovery of the action of magnetism on light, and considered that the department of magneto-optics was likely to be fruitful in discoveries. He seems to have detected a relation between the rotary magnetic power and the index of refraction of substances, the function being $\mu\sqrt{(\mu^2-1)}$, which he claims approximately for bodies belonging to the same chemical family. This was published in 1875. He found, however, afterwards that the law for magnetic substances is quite different from that for diamagnetic, the negative rotations varying approximately, not as the inverse square, but as the inverse fourth power of the wave-length, and, in the case of dissolved magnetic substances, as the square of the concentration.

Up to that time the Faraday effect had not been observed in gases, but with this law as a clue he was able to realise the magnitude of the effect to be expected in their case; and in 1878–1880 he demonstrated that gases enjoyed the same rotatory power as liquids and solids—oxygen, however, on account of its magnetic properties, being anomalous.

He was accordingly interested in the influence of terrestrial magnetism on the atmosphere, especially on the effect of a great thickness of magnetised oxygen on light; and as a preliminary he determined the intensity of the earth's magnetic field by its action on carbon disulphide. Moreover, at the International Congress on Electric Units he proposed this as an absolute standard of current strength.

He developed some theoretical views as to the cause of magneto-optic phenomena, and became specially interested in the discovery of Zeeman. The interest of this, indeed, deflected him for a time from his researches in radioactivity—which he had just himself discovered—since he thought that the Zeeman effect corresponded exactly with that magnetic molecular action which he had been looking out for; and he illustrated magnetic rotation, the Zeeman effect, and anomalous dispersion, by an ingenious experiment on sodium vapour. Electrons seemed to him just to fill the lacuna between ether and matter, and so to be of value in sustaining the vortex or spinning theory of magnetism which he favoured.

He seems to have told his son that he had looked for the Zeeman effect in 1888, as indeed Faraday had before him; but, in both cases, without theoretical guide, and without being aware of the kind of magnitude which they must be able to detect.

(Sir J. Larmor had anticipated the effect theoretically, but, supposing radiation at that time to be due to atoms rather than electrons, had found the calculated effect too small for observation. He had, in fact, corresponded with me on the subject, and, stimulated by him, I repeated Zeeman's experiment, and showed it at a *soirée* of the Royal Society immediately after the Amsterdam discovery.)

In 1879 H. Becquerel published a memoir on magnetic details in nickel and cobalt, and showed that ozone was more magnetic than oxygen; whilst nickel-plated iron became curiously magnetic after having been heated to redness.

With his father he made many experiments on the temperature of the underground soil, and verified Fourier's theory for the case of underground temperature.

He applied a discovery of his father in 1873—namely, that infra-red rays were able to extinguish certain kinds of phosphorescence—to a study of the bands of the infra-red solar spectrum, and likewise to the spectra of other substances, in particular of water, of the atmosphere, and of rare earths; likewise of numerous metallic vapours. The new field thus opened to spectrum analysis must have covered a range of wave-length more extensive than the whole of the luminous region and of the ultra-violet portion at that time known (1883–1884).

He specially examined the phosphorescence of uranium salts, and studied the spectrum of their phosphorescence which his father had discovered, attempting to give the law of distribution of these bands. The non-phosphorescent salts of uranium appear to have absorption bands governed by the same law, revealing an exceptional molecular constitution.

He studied the absorption bands of a great number of minerals, attending specially to the spectrum of didymium which Bunsen had observed in 1866, together with their variation with the plane of polarisation of the incident light.

From all this he argued that the absorption of a molecule is independent of the action of neighbouring molecules, and goes on as if the absorbing molecule were alone; so that if a crystal exhibits absorption bands corresponding with its various directions other than the axial directions, it must mean that other substances are present. The occurrence of neodymium and praseodymium verified these deductions.

Becquerel considered that this method of absorption spectra, applied to crystals, conferred upon the observer a power of mapping out their intimate constitution; and he likens it to observing the arrangements of furniture and movements of people who dwell in a glass house.

Some years later (1891) he described for the first time the spectra of the phosphorescence emitted by minerals when they are heated; and, by differences of duration and brightness, considered that he could detect different components; thus, in the natural course of things, he was led to his fundamental and most brilliant discovery, with which physicists have been concerned ever since.

Personal Account of his Chief Discovery.

The following is a paraphrase of Henri Becquerel's own account of the matter:

The idea of examining whether bodies could emit an invisible and penetrating radiation was suggested to me by the announcement of the first experiments of Röntgen. Poincaré showed the first radiographs of Röntgen at the Academy of Sciences in Paris on January 20th, 1896, and in answer to a question from me [Becquerel] stated that the source of the rays was the luminous spot on the wall of the glass tube which received the cathode stream. I immediately thought of examining whether this new emission was caused by the vibratory movement which gave rise to the phosphorescence, and whether all phosphorescent bodies could emit similar rays. At this epoch no one imagined it a spontaneous production of energy; it was natural to suppose that a transformation of energy must be going on. In other words, that energy must be supplied in order to get the radiation.

Becquerel seems to have mentioned his project to Poincaré, and to have begun a series of experiments the very next day. On January 30th Poincaré wrote in the *Revue Générale des Sciences* an article on Röntgen rays, in which he said:

"Thus it is the glass which emits the rays, and it emits them by becoming fluorescent. May we not ask, therefore, whether all bodies whose fluorescence is sufficiently intense may not emit beside luminous rays the *X*-rays of Röntgen, whatever may be the cause of their fluorescence? These phenomena would then be no more [necessarily] connected by [being the consequence of] an electric stimulus. It may not be very probable, but it is possible, and doubtless easy enough to verify."

This pronouncement seems to have started a considerable number of experiments.

Thus, for instance, M. Charles Henry placed on a photographic plate, enveloped in black paper, an iron wire with a few coins, and on one of the coins some phosphorescent zinc sulphide, and exposed the whole to Röntgen rays. On developing the radiograph he found that the shadow of the iron wire appeared lighter under the coin covered with zinc sulphide, and concluded that that substance had emitted rays through the metal on to the photographic plate. The experiment, however, was not convincing, and has not been confirmed. M. Henry made other experiments, such as one on the action of the rays emitted by hexagonal blende across leaves of aluminium and cardboard—an experiment subsequently developed by M. Troost.

Some experiments seem also to have been made by Monsieur Le Bon, which, however, M. Becquerel mentions only to discard, since he considers that they have been wrongly associated with his new phenomenon. They have to do with rays from luminous sources said to be capable of traversing metallic screens, but stopped by black paper. Henri Becquerel considered them all due to known causes, but to be arranged and described in so confused a manner as to mask the real reason of the observed facts; he says that it suffices to re-read, in the *Comptes rendus*, M. Le Bon's first publications to convince anyone that the author had no idea of the phenomenon of radioactivity. M. le Bon's experiments were also reviewed by MM. Niewenglowski, Lumière, and Perrigot, and were shown to have been due to infra-red rays—which are known to be able to traverse ebonite. Becquerel himself verified the completeness of these explanations, but says that one note of Monsieur Niewenglowski deserves attention, namely, this: A screen covered with powdered calcium sulphide, after having been exposed to light, emits radiations which are able to impress a photographic plate through cardboard and black paper; and Becquerel goes on to say that he has repeated similar experiments, which are remarkable—possibly indicating the presence of either infra-red or ultra-violet rays of penetrating character—but that the phenomenon does not appear to be the same as that which constitutes radioactivity.

His own first observations on the radiating properties of the salts of uranium were published at the sitting of the Academy of Sciences on February 24th, 1896.

In the first series, photographic plates enveloped in black paper were exposed to the radiation of phosphorescent substances stimulated in vacuum tubes too slightly rarified to give X-rays; but the exposure given was insufficient to show any result.

In another series, bodies such as fluorspar, hexagonal blende, etc., excited in ordinary air by sparks, were applied to a covered photographic plate in the same way; but still they gave no result, either during or after excitation, although the exposure lasted several hours. He says he hesitated to try some beautiful preparations of phosphorescent sulphides or other salts which he possessed, in these circumstances, because of their deliquescence.

Nevertheless, in spite of the negative results obtained so far, he still built great hopes on experimentation with uranium salts, of which he says: I had formerly many opportunities of studying their phosphorescence as a sequel to the work of my father. These bodies, he goes on, appear to have a peculiarly remarkable molecular constitution, regarded from the point of view of phosphorescence and absorption.

Among the preparations of uranium salts in his possession there were some beautiful plates of the double sulphate of uranium and potassium, which he had prepared about fifteen years before. These crystals, unalterable in air, seemed entirely suitable for the projected experiment, but he happened to have lent them to his friend, Monsieur Lippmann, in connexion with his researches on interferential photography, of which the beautiful results are well known. The same day, however, on which M. Lippmann returned those crystalline plates, Becquerel made the first successful observation; whence originated the whole series of his radiographic positive results.

He placed two crystals of the double sulphate on a photographic plate enveloped in a double sheet of thick black paper, putting under one of them a piece of silver; then he exposed the whole to the sun—a procedure which subsequent knowledge showed to be entirely useless—and after some hours developed the plate, and saw a light impression corresponding with the silhouettes of the crystals, and a shadow of the piece of silver. The luminosity of uranium salts ceases in the one-hundredth of a second after exposure to light, so that it appeared quite necessary to maintain the luminous stimulus during the attempt.

He then repeated the experiment, interposing a thin sheet of glass or of mica in order to stop anything due to vapour or other chemical emanation. The same result was obtained, only feebler. These were the results communicated by him to the Academy of Sciences on February 24th, 1896.

On March 2nd, 1896, he described further experiments, where he showed that plates protected by aluminium 2 millimetres thick were not affected at all by a whole day's exposure to the sun unless a crystal of the uranium salt was added.

Other simple variations were described, and then came the opportunity for discovery. He usually affixed the uranium salt to the aluminium or other opaque coating by strips of gummed paper. He prepared some in this way on Wednesday the 26th and Thursday the 27th of February, and as on these days the sunlight was very intermittent, and the exposure quite unsatisfactory, he preserved the plates, fully prepared for subsequent treatment, in a dark cupboard, without developing them or removing from them the crystals of uranium. Fortunately, however, the sun did not shine on either of the two following days, and so he developed the plates on March 1st, expecting to find only very feeble impressions. On the contrary, they came out stronger than he had seen them before, and he perceived that the action had continued in the dark. He announced this fact to the Academy of Sciences at its sitting on March 2nd, and naturally proceeded to repeat the whole of the experiments without any exposure at all, subsequently concluding thus:

It thus appears that the phenomenon cannot be attributed to luminous radiations emitted by reason of phosphorescence, since, at the end of one-hundredth of a second, phosphorescence becomes so feeble as to become imperceptible.

So he announced the fundamental new fact of the emission of penetrating rays without apparent exciting cause. Either the diffuse light had long stored its energy in these substances, or else there was some phenomenon of a completely new order. In the first case the effect must gradually decay with time; and it was to the examination of that possibility that his next series of experiments were directed. He proceeded to keep crystals in complete darkness for years, and naturally the complete disproof of the alternative or slow decay hypothesis was a matter of time. Suffice it to say that although the cause of the phenomenon was not then ascertained, the fact of apparently spontaneous radioactivity was definitely established.

It is doubtful whether with uranium salts alone anything more than a small fraction of our present knowledge of radioactivity could have been attained; but very soon after the first discovery, namely, on March 7th, 1896, Becquerel made the important and practically useful observation that the new radiation had the power of discharging electrified bodies, that is, of rendering the surrounding gas a conductor. He employed a gold-leaf electroscope, of which the leaves were examined by a microscope, and measured their rate of subsidence under the influence of various salts. The comparative ease and rapidity and metrical character of this method of examination induced Madame Curie to take as the subject of her Doctorial Thesis the measurement of the radioactive powers of an immense number of minerals, and so led her gradually to one of the most brilliant and striking discoveries of modern times, the whole representing a new epoch in our knowledge of atoms, and therefore in physico-chemical science.

Work of the Becquerel Family.

The name "Becquerel" is so familiar to students of physics, and it seems so natural that the name should occur in connexion with physical investigations throughout the past century, that we are rather apt to take the work for granted and neglect consideration of the personality behind the work. Moreover, when there are three or four workers of the same name, some care is needed to discriminate the individual.

As this is a Becquerel Lecture it may be convenient here, therefore, to make a kind of summary of the work of this eminent family, especially as they constitute a group notable from the point of view of Galtonian heredity.

The present Professor of Physics in the Natural History Museum in Paris, Monsieur Jean Becquerel, has made a convenient summary of the work of his ancestors, that is to say, of his father, grandfather, and great-grandfather, in an inaugural Address which he gave on the assumption of his inherited Chair; and this I shall make use of in the summary that follows.

The earliest and most prolific of the group of four was Antoine-César Becquerel, who, in the course of an exceptionally long life devoted wholly to Science, made a series of familiar discoveries, of which we are too apt to forget the origin. They lay chiefly in the direction of the voltaic pile, electrometallurgy, and the applications of electrical knowledge to natural history, meteorology, and agriculture.

His son, Edmond Becquerel, succeeded him, and his researches are mainly connected with photography, spectroscopy, and phosphorescence.

Work of Antoine Becquerel.

The work of Antoine César Becquerel may be thus briefly summarised:

In 1819 Antoine Becquerel seems to have investigated piezo-electricity, or the electric manifestation displayed by minerals under pressure, generalising the observations of the Abbé Haüy very considerably; thus it was that he was led from the subject of mineralogy to that of electricity.

In 1823 he worked at thermo-electricity and the seat of the *E.M.F.* in a voltaic pile, being a strenuous supporter of what was called the chemical theory, and arguing against Volta and Davy.

In 1825 he was comparing the electric conductivity of different metals, and devised the first differential galvanometer for the purpose.

In 1829 (nine years apparently before Daniell) he invented a constant battery, explaining why the power of the ordinary voltaic cell fell off so rapidly, owing to deposits on the plate, and indicating the necessity of dissolving or avoiding such deposits. So he says the best results are obtained when the copper is plunged into a solution of copper nitrate, and the zinc into a solution of zinc sulphate; the two being separated by a membrane of gold-beaters' skin. A pile so constructed, he says, with each metal plunged into a separate vessel enclosing a suitable liquid, avoids the ordinary polarisation of the plates, whereby currents tend to be produced in the inverse sense to the main current. Professor Becquerel now says that sulphate of copper was as often used by his ancestor as the nitrate, and that this constant battery was then called a *pile cloisonnée*; although in an improved and more practical form it became universally known subsequently as the Daniell cell.

In 1846 he constructed the first silver chloride cell; and in the year following invented an electromagnetic balance for measuring electric currents—a glorified edition of which, designed by Viriamu Jones and W. E. Ayrton, is now set up at the National Physical Laboratory under Dr. Glazebrook at Bushey.

For forty years his work lay in the direction of applying his electrical knowledge to natural history, to agriculture, and to physiology. He also considered electrical effects in meteorology and other terrestrial manifestations; attending also to such subjects as the climatic effect of forestry on rainfall.

In 1850 he worked in electro-metallurgy, studying the deposits of many kinds of metals, and the conditions under which they could be obtained; among other things finding how to deposit nickel and cobalt.

In 1867 he discovered the phenomenon of electro-capillarity, and demonstrated its influence in connexion with endosmose and exosmose. He doubted the existence of the muscular currents discovered by Du Bois Reymond, and ultimately attributed them to capillary causes. He found an *E.M.F.* between different liquids separated by porous diaphragms; and at the age of eighty-seven he considered all this in relation to the phenomena of *life*.

He died in January, 1878, and only a few months earlier, at the age of ninety, published his last work, on the *E.M.F.* and the heat production of electro-capillary actions.

Work of Edmond Becquerel.

Some idea of the work of Edmond Becquerel can be thus given:

Edmond Becquerel, born 1820, became, at the age of eighteen, assistant to his father; and, stimulated by the discoveries of Daguerre, studied the production of electricity by light, and endeavoured to make an electro-chemical actinometer. Among other photographic discoveries he photographed the ultra-violet spectrum in 1842, and began the photography of colours. His coloured photographs had to be kept in the dark, where they have lasted seventy years, but they cannot be exposed to even diffuse daylight.

In 1843 he studied Joule's law of heat production by electric currents in liquids, and made a liquid rheostat for use with a differential galvanometer to measure liquid conductivities.

In 1846 he examined Faraday's magnetic rotation of light, showing that it varied inversely as the square of the wave-length, and he verified the magnetic properties of oxygen.

In 1853 he investigated the conductivity of hot gases, and measured furnace temperatures by photometric means, showing that they were not so high as had been supposed. (A development of this method has since been applied to the temperature of sun and stars.) He also constructed a thermo-electric pile with about one-third of a volt *E.M.F.*

But the work for which he is chiefly known is that on phosphorescence. This had been begun by his father in 1839; the phosphorescence having been excited by electric discharges.

In 1843, in his work on the ultra-violet spectrum, he examined its phosphorescent influence, and thus saw the dark lines in that region of the spectrum which he had already discovered by photography.

In 1857 he described the preparation of many phosphorescent substances, with the region of the spectrum appropriate for exciting each. He also excited them by the induction coil, and in 1858 invented that beautiful instrument *the phosphoroscope*, with which naturally he made many observations.

In 1859 he showed that rarefied oxygen remained luminous some instants after the passage of a discharge—a phenomenon which, in the case of nitrogen, has been so admirably pursued recently by our Professor Strutt.

In 1869 he published a work on phosphorescence called "Light, its Causes and Effects," in two volumes; which book is said by Professor Becquerel to have been full of suggestions to young physicists on almost every page.

In 1872 he began to examine the phosphorescent properties of uranium, and in 1873 devised a method of studying the infra-red rays of the spectrum, by their power of extinguishing the phosphorescence of a screen coated with hexagonal blende on which they fell. This became the basis for his work in making isochromatic plates by the use of different absorbing substances and of chlorophyll; and, throughout, he applied his researches to meteorology and to the action of light on vegetation.

Conclusion.

The experimental labours of Henri Becquerel, based on the work of his predecessors, has been already dealt with. It lies chiefly in the domain of phosphorescence and spectroscopy, especially the absorption spectra of crystals. He concerned himself also with magneto-optics, and was the discoverer of the spontaneous radioactivity of matter.

Professor Jean Becquerel concludes his Address with some useful remarks on matters of general interest, especially concerning the association of a Chair of Physics with a Museum of Natural History. It appears that the creation of such a Chair was judged useful in 1838, after some of the work of his great-grandfather. A small and modest laboratory was then established, devoted to pure physics for the sake of its possible application to natural history of the most general kind. The discovery of radioactivity alone would have justified such a foundation, for the influence of that material property is now known in the ground, in mineral waters, in the atmosphere, and in geological formations; likewise in biology and medicine the rays have proved of high interest. But, as can be deduced from the preceding summary, a great many other applications and practical consequences have followed from the researches conducted in that small laboratory.

Professor Becquerel claims that one of the causes conducive to the productiveness of this laboratory was the continuity of the work accomplished there. Antoine Becquerel began the study of phosphorescent substances under electric discharge. Edmond Becquerel continued the work, and recognised the exceptional properties of the salts of uranium. Henri Becquerel pursued the subject, and effected the climax. He himself definitely recognised the long tradition of pertinacious and successful inquiry on which he had built, and he spoke thus:

It was perfectly appropriate that the discovery of radioactivity should have been made in our laboratory, and if my father had lived in 1896 he it is who would have made it.

CCXV.—*Studies of the Constitution of Soap in Solution: Sodium Myristate and Sodium Laurate.**

By James William McBain, Elfreida Constance Victoria Cornish, and Richard Charles Bowden.

One of the most interesting classes of substances the constitution and physical properties of which require elucidation is that of electrolytic colloids. This class includes many well-known substances, such as soaps, dyes, indicators, tannin (which is a weak acid coming between carbonic and acetic acids), protein salts, many hydrolysed salts, for example, chromic and ferric derivatives, silicates, etc. The recognition of these substances as constituting a class by themselves is of recent origin, having arisen essentially out of the physico-chemical study of such materials as casein, soap, and Congo-red. Their particular interest lies in the fact that they exhibit electrolytic and colloidal properties to an equal extent, since they contain both electrolytic and colloidal constituents.†

Presumably, in each of these cases we are dealing with simultaneous electrolytic, colloidal, and hydrolytic equilibria. In no case

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* Previous papers: J. W. McBain and M. Taylor, *Ber.*, 1910, **43**, 321; *Zeitsch. physikal. Chem.*, 1911, **76**, 1; R. C. Bowden, Trans., 1911, **99**, 191.

† The idea has been more or less current for a decade; the term itself is due to W. B. Hardy (*Gedenkboek van Bemmelen*, 1910, 180), who, however, employed it to express the definite assumption that the anion in soap solutions is colloidal. Here the term is used in a broader sense without prejudging the question as to the exact nature of each constituent present.

have the physico-chemical relationships been sufficiently investigated.

The soaps were selected for systematic study because of the apparent simplicity of their chemical nature and their accessibility to study from various points of view.

The study of these relationships is of the first importance in view of the question of the experimental transition of a colloid into a crystalloid, and the conditions under which this takes place. Many of the most eminent authorities deny its possibility, and the work hitherto carried out, for example, that in this laboratory on soap solutions, is capable of interpretation either from the point of view that gradual transition does take place* or (present working hypothesis) that strictly colloidal and strictly electrolytic constituents co-exist and merely vary in relative amount. A decision between these two opposite opinions would seem to be of fundamental importance for the interpretation of colloidal phenomena in general.

In the case of soaps one of the most striking results already obtained was the anomalous conductivity-curve with the dilution, which possessed both a maximum and minimum; in the case of sodium palmitate the maximum was in $N/2$-solution, the minimum between $N/5$ and $N/10$. In the case of sodium stearate the maximum was in N-solution, the minimum between $N/2$ and $N/10$. The peculiar shape of the conductivity-curve was tentatively accounted for as being due to the changes in the degree of dispersion of the colloid and in its amount, the assumption being made that the only colloids present were acid sodium salts. Hydrolysis predominates in very dilute solutions, and in highly concentrated solutions there is presumably a great deal of normal salt formed, but its dissociation and conductivity would be relatively low, and it may even be colloidal and hence non-conducting. In intermediate solutions, the colloidal acid salt assumes so high a degree of dispersion (as is evident from the appearance of the solutions) that its sorptive powers are probably diminished, which would set free sodium hydroxide and account for the maximum in conductivity.

The effect of varying the amount of sodium hydroxide is in accordance with the hypothesis just outlined. The next step is obviously to vary the nature of the soap still further by taking the next lower homologues and observing how the shape of the conductivity-curves and the position of maxima and minima alters with diminishing molecular weight of the acid radicle.

This possesses a further source of interest in that the lowest members of this homologous series do not give rise to colloids at

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* Compare the frequently met with hypothesis that ions may be colloidal.

all. An essential part of all these conductivity determinations remains that, contrary to previously accepted doctrine, the conductivities are high throughout.

EXPERIMENTAL.

The experimental method is that described by McBain and Taylor (*loc. cit.*) for solutions of sodium palmitate. They found that the conductivity of each concentration was perfectly definite, no matter how the solutions were made up; hence it was safe to make the same assumption in the case of this lower homologue.

Solutions were made from sodium hydroxide free from carbon dioxide, the correct amount of myristic or lauric acid being weighed into the silver tubes used for the experiments. These were sealed with cap and ring of pure silver by means of heavy clamps, and the solutions shaken at 90° until they became homogeneous. This does not take long, as they differ entirely from the highly viscous sodium palmitate solutions. The conductivity was determined by inserting dipping electrodes of Jena-glass according to the Kohlrausch method. The constant of the cell, owing to the silver tubes used, varied with the resistance of the solutions measured. They were determined by plotting the results obtained from N-, $N/10$- and $N/100$-potassium chloride solutions. The myristic and lauric acids (Kahlbaum) melted, not sharply, at 53·4° and 42·9° respectively. The lauric acid was recrystallised until it melted at 43·05°. All vessels and instruments were carefully calibrated and standardised.

Densities.

Densities were determined in pyknometers of about 5 c.c. capacity, so mounted that they were entirely immersed in the thermostat until the final adjustment was complete. Each result is the means of several determinations differing by a few units in the fourth decimal place. In the case of the myristate the density was found to be D_4^{90} 0·9678. This differs by only 0·25 per cent. from that of water (0·9653) at the same temperature, and hence the values for the other concentrations could be estimated with sufficient exactness by linear interpolation.*

The solutions of sodium laurate contained about 3·5 per cent. less sodium than was intended (see below); as the concentrations refer to the weight-normality of the laurate radicle, the density of the N-solution should be roughly 0·0020 higher. The series, however, is comparable within itself.

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* Densities and older series of conductivity values of sodium laurate by R. C. Bowden, all other measurements in this communication by J. W. McBain and E. C. V. Cornish.

TABLE I.

Density of Sodium Laurate.

Concentration..	1·0	0·5	0·2	0·1	0·05	0·01
D_4^{90}	0·9711	0·9693	0·9678	0·9669	0·9668	0·9660
D_{90}^{90}	1·0060	1·0042	1·0026	1·0017	1·0015	1·0008
D_4^{25}	—	—	—	—	0·9984	0·9973
D_{25}^{25}	—	—	—	—	1·0014	1·0003

The results at 90° make a smooth curve, the difference between the observed density and that of water not increasing as fast as the concentration. F. Goldschmidt (*Zeitsch. Elektrochem.*, 1912, **18**, 386), using the potassium salt of the acids from palm kernel oil (said to be essentially potassium laurate), obtained values more nearly proportional to the concentration and distinctly larger than ours for the higher concentrations; thus, 1·001 for *N*/20, 1·004 for *N*/5, and 1·015 for *N*. He also obtained a distinct increase in density as referred to water of equal temperature when the measurements were carried out at 20°, although this relative increase did not exceed 0·5 per cent. The present results for the pure sodium salt, however, appear to indicate that the coefficient of expansion at least in the dilute solutions is the same as that of water (within 0·05 per cent.); thus it is possible without appreciable error to obtain the values for intermediate temperatures by using the coefficient for water; this we have done in the case of sodium myristate in calculating the conductivity. It may be noted that solutions of sodium stearate, C_{18}, and palmitate, C_{16}, are lighter than water, whilst the myristate, C_{14}, laurate, C_{12}, and acetate, C_2, are heavier, the differences being roughly in proportion to the position in the homologous series.

Conductivity.

The following table gives the experimental results for sodium myristate solutions at 90°. The first column gives the weight-normality; the second, the number of grams of sodium myristate to 100 grams of water; the third the number of the electrode; the fourth the cell constant; the fifth the specific conductivity; the sixth the average specific conductivity; the seventh the densities (obtained by interpolation, see under), and the last column the molar conductivity at 90°. The molar conductivity is derived by multiplying the weight of solution containing 1000 grams of water by the specific conductivity, and dividing by the weight-normality and the density. In each case all the corrections enumerated by McBain and Taylor were applied. The absolute values of the conductivities, except in the cases specified, we may regard as accurate to about 2 per cent., the relative values to about 1 per cent.*; thus the present results do not pretend to the painstaking accuracy of the sodium palmitate measurements, where equilibrium was approached from both sides, and where, further, each result was checked by many independent measurements.

TABLE II.

Conductivity of Sodium Myristate at 90·00°.

I.	II.	III.	IV.	V.	VI	VII.	VIII.
1·500*N*	37·5	XIII	3·011	0·0899	0·0896	(0·9690)	84·76
		XII	5·094	0·0893			
1·000*N*	25·0	XIII	3·010	0·0735	0·0735	0·9678	94·93
		XII	3·096	0·0737			
0·750*N*	18·75	XII	3·097	0·0594	0·0596	(0·9671)	97·57
		XIII	3·008	0·0598			
0·500*N*	12·5	XIII	3·008	0·0422	0·0426	(0·9665)	99·15
		XIII	3·008	0·0429			
0·2000*N*	5·00	XIII	2·992	0·01744	0·01752	(0·9658)	95·23
		XII	3·113	0·01761			
0·1000*N*	2·50	XIII	2·985	0·00914	0·00909	(0·9655)	96·51
		XII	3·404	0·00904			
0·0500*N*	1·25	XIII	2·978	0·00522	0·00526	(0·9654)	110·4
		XIII	2·978	0·00534			
		XIII	2·978	0·00522			
0·01000*N*	0·250	XIII	3·033	0·001829	0·001846	(0·9653)	191·7
		XII	3·034	0·001863			

Table III gives the corresponding data for sodium laurate at 90°. The data for 0·1, 0·5, and 1·0*N* are obtained from a previous complete series for the solutions the densities of which were recorded above. From the new determinations for the 0·01, 0·05, 0·2, and 1·5*N*-solutions it was apparent that the values for the previous solutions which had been made up by mistake to a wrong standard had to have their specific conductivity increased by 9·0 per cent. This has been done in the table. This decrease in conductivity, due to a lack of more than 3 per cent. of sodium, is in accordance with the effects obtained in the numerous measurements made with sodium palmitate with excess and deficiency of alkali (J. W. McBain and M. Taylor, *loc. cit.*).

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* It has already been pointed out (J. W. McBain and M. Taylor, *loc. cit.*, p. 196) that quite careful measurements of ordinary salt solutions at this temperature are not generally more accurate than this, and at room temperature, even Kohlrausch's measurements for acids and bases are incorrect by several units per cent.

TABLE III.

Conductivity of Sodium Laurate at 90·00°.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1·500*N*	33·3	XII	3·042	0·1057	0·1054	(0·9740)	96·2
		XIII	3·012	0·1051			
0·982*N*	21·83	XIII	3·006	0·0820	0·0816	0·9711	104·2
		XIII	3·006	0·0812			
0·496*N*	11·01	XIII	3·005	0·04741	0·04742	0·9693	109·5
		XIII	3·005	0·04743			
0·2000*N*	4·44	XIII	3·002	0·02101	0·02104	0·9678	113·4
		XII	3·058	0·02107			
0·0998*N*	2·218	XIII	2·998	0·01187	0·01185	0·9669	125·5
		XIII	2·998	0·01183			
0·0500*N*	1·111	XIII	2·982	0·00750	0·00751	0·9668	157·0
		XIII	2·982	0·00751			
0·01000*N*	0·2222	XIII	2·956	0·001893	0·001870	0·9660	193·9
		XII	3·033	0·001846			

On comparing these values for sodium laurate with those of Goldschmidt (*loc. cit.*) for impure potassium laurate (173·5 for 0·05*N*, 135 for 0·191*N*, 141 for 0·5*N*, 137·2 for 1·02*N*, and 116·2 for 1·4*N*), his values are seen to be uniformly higher. Further, his values go through a maximum and a minimum, whilst the sodium salt exhibits merely a "step out." This is surprising, since potassium soaps on account of their greater solubility and insensibility to the precipitating action of electrolytes are expected to behave more like normal electrolytes.

The results in the tables above are compared with corresponding results obtained in this laboratory for sodium palmitate, sodium stearate, and sodium acetate in the following table.

TABLE IV.

Molar Conductivities of Sodium Salts at 90·00°.

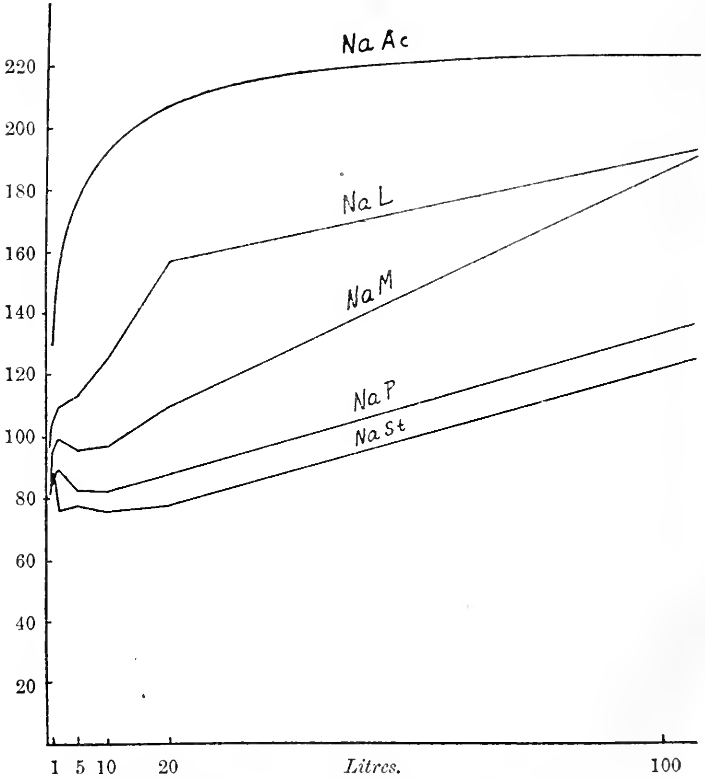
Concentration.	1·5	1·0	0·75	0·50	0·35	0·20	0·10	0·05	0·01
NaStr C_{18}	81·5*	88·3	—	76·1	—	77·4	76·0	78·0	125·9
NaP C_{16}	84·5	84·66	87·48	89·48	87·04	82·38	82·51	88·61	137·7
NaM C_{14}	84·8	94·9	97·6	99·2	—	95·2	96·5	110·4	191·7
NaL C_{12}	96·2	104·2	—	109·5	—	113·4	125·5	152·0	193·9
NaAc C_2	—	129·7	—	—	—	178·9	195·0	—	228·2

* Two independent measurements by Miss Taylor; the actual data were: weight-normality, 1·451*N*; grams per 100 grams of water, 44·44; electrode No. IX; cell constant, 3·44 and 3·2; specific conductivity, 0·0781 and 0·078; estimated density, 0·950; molar conductivity, 81·5. The solution is a viscid gum; an accurate measurement would require special study. This suffices to show that the maximum lies near 1·0*N*.

From this table and the accompanying graphs, it will be seen how very similar, both in magnitude and behaviour, are the results obtained with sodium myristate and sodium palmitate in all but the 0·01N-solution.

This is unexpected and somewhat remarkable, since the solutions themselves are quite dissimilar in consistency, and even in appearance, the palmitates being viscid, gummy solutions, whilst all the myristates, even the N-solution, are quite mobile at 90°. Also the fact that the conductivity diminishes regularly as one ascends the homologous series, is not what would have been expected, since the conductivity is probably largely due to free sodium hydroxide, and the stearates are always assumed to be most hydrolysed. Consequently the stearates should give a higher conductivity than the palmitates, etc., particularly in dilute solution, whilst the contrary is the case. According to this view it is evidently necessary to assume that sorption operates in the opposite direction, being

Fig. 1.

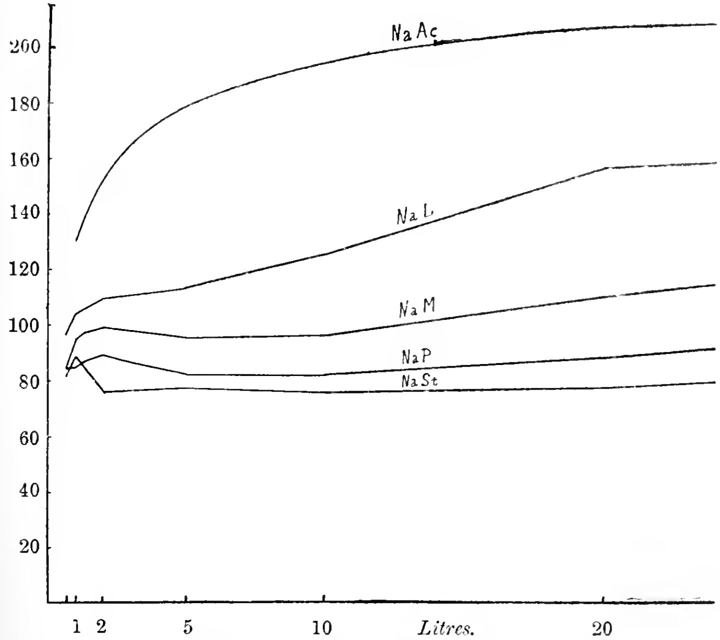


Molar conductivities of sodium salts of fatty acids at 90°.

greatest for the stearate. It is not certain that stearic acid is appreciably weaker than, say, lauric acid; increased hydrolysis would, therefore, have to be ascribed to the increasing insolubility of the products of hydrolysis (not the acids themselves).

On comparing the positions of the maxima and minima in the molar conductivities of the homologues (see graphs), it is evident that the chief feature is the development in the extent and importance of the depression imposed on the curve at $N/5$ ($N/2$ to $N/10$) as we pass down the homologous series from the stearate.

Fig. 2.



Molar conductivities of sodium salts of fatty acids at 90°.

The depression in the curve for the stearate extends from $N/2$ to $N/20$, whilst in the lower members of the series the maximum is attained in $N/2$-solution, although in the case of the laurate the depression is not great enough to produce a maximum.

Equally significant is the fact that this depression seems to be imposed on each curve at about the same region of concentration. This is very surprising, since one would have expected a pronounced displacement as the number of carbon atoms in the acid decreased, a change in concentration making up for a falling off in colloidal properties. We expect to extend these measurements to the other homologues and to the potassium salts.

Effect of Temperature on the Conductivity-curve.

It seemed desirable to estimate the effect of temperature on the shape and position of the curve for, say, sodium myristate, as all the results hitherto have been determined at 90·0°. One might quite well expect to find that the temperature-coefficients would also exhibit anomalous changes with the concentration, and thus the conductivity-curve and the equilibria underlying it would depend very much on the temperature.

The following are the experimental results for the temperature-coefficients. They were obtained by taking solutions of each concentration, measuring them at 90·0°; then, without removing the electrode, measuring them at successive temperatures. The results italicised were obtained from duplicate solutions measured successively at 90·0°, 80·0°, 90·0°, 80·0°, 90·0°, 70·0°, 90·0°, 70·0°, 90·0°, 60·0°, 90·0°, 60·0°, 90·0°, 50·0°, 90·0°, 50·0°, 90·0°, etc. In accordance with the results of a preliminary study, periods ranging from six hours at 40° to three-quarters of an hour at 80° were allowed for the conductivity to adjust itself to its final value, although even at 40° the results would have been correct to within 1 or 2 per cent. within one hour. McBain and Taylor, who worked only at 90·0°, found the conductivity to be independent of the time. In the light of these new results, this is evidently due to their having worked at the highest temperature. The significance of their discovery, that the conductivity assumes a true reversible equilibrium value, is not impaired, but rather augmented, by the fact that the equilibrium conductivity at lower temperatures is attained only after the lapse of a measurable period.

For some reason, the conductivity requires more and more careful measurement in order to obtain trustworthy results as the temperature is lowered; thus the temperature-coefficients at 50·0° are uncertain to the extent of several units per cent. It was noticed that the conductivities at 90·0° did not change very much, except in the case of more dilute solutions, in spite of the prolonged exposure to the Jena-glass of the dipping electrodes during the treatment outlined above. In table V the results are expressed in terms relative to the specific conductivity at 90·0°, which is taken as unity for each concentration.

Table V.

Weight-normality.	90°.	80°.	70°.	60°.	50°.	40°.
1·5	1·000	*1·121*	*1·279*	*1·505*	—	—
1·0	1·000	*1·118*	*1·273*	*1·498*	1·800	—
0·5	1·000	*1·126*	*1·308*	*1·560*	*1·872*	—
0·2	1·000	1·118	1·311	1·545	1·861	2·40
0·1	1·000	1·132	1·311	1·559	—	—
0·05	1·000	1·126	1·312	1·599	1·863	2·22
0·01	1·000	1·126	1·316	1·547	1·853	less than 2·35

These results have been smoothed out as shown in table VI:

Table VI.

Weight-normality.	90°.	80°.	70°.	60°.	50°.	40°.
1·5	1·00	1·121	1·279	1·505	—	—
1·0	1·00	1·118	1·272	1·498	1·800	—
0·5—0·01	1·00	1·126	1·311	1·561	1·862	2·32

Using table VI, the molar conductivities of sodium myristate for varying temperatures become the following, as shown in table VII, where the coefficient of expansion with the temperature has been taken into account, taking it equal to that of water.

Table VII.

Molar Conductivities of Sodium Laurate Solutions at Various Temperatures.

Weight-normality.	90°.	80°.	70°.	60°.	50°.	40°.	25°.
1·5	84·8	75·1	65·4	55·2	44·8	—	—
1·0	94·9	84·3	73·6	62·2	51·5	—	—
0·5	99·2	87·5	74·6	62·3	52·1	—	—
0·2	95·2	84·0	71·5	59·8	50·0	40·0	—
0·1	96·5	85·1	72·6	60·6	50·7	40·5	—
0·05	110·4	97·3	83·1	69·4	58·0	46·4	(34·6) (see under)
0·01	191·7	169·0	144·3	120·5	100·6	80·3	—

The results in tables VI and VII show that the effect of temperature on the anomalous shape of the conductivity-curve is quite unimportant, although there is a very slight tendency for the maximum to move towards a higher concentration at lower temperatures. The latter result is in accordance with the single series of measurements of F. Goldschmidt (*loc. cit.*) for the potassium salt of the fatty acids of palm kernel oil at 90° and 20°.

It is interesting to note that Goldschmidt observed a time lag of several units per cent. in the adjustment of the viscosity of his solutions when suddenly cooled from 90° to 20°, although no mention is made of a similar result having been looked for in his conductivity measurements at 20°. The initial viscosity observed when his solutions were cooled from 90° to 20° was greater than that attained on further keeping at 20°; in other words, starting from 90° the viscosity of his solutions must have risen enormously and then have diminished slightly. This is exactly analogous to our own observations in the case of conductivity, where the after-effect is of the order of magnitude of 1 per cent., although often it is not observed at all. If the conductivity has been decreased by changing, say, from 90° to 50°, the conductivity after the first hour is rising slightly; similarly, the conductivity falls slightly after a solution has been at 50° for some time after bringing it from room temperature (liquid or solid).

The exact significance of these residual phenomena is not clear, although evidently one of the minor subsidiary equilibria is displaced towards low conductivity and high viscosity at higher temperatures. Possibly it may be found to be an absorption property of the colloids present (as distinguished from adsorption). Goldschmidt's qualitative observations would make it appear a supersaturation in the state of coagulation or dispersion of the colloids present. Against this may be urged that in the case of conductivity it occurs both with rising and falling temperatures, and, further, data below show that coagulation acts in the opposite direction, since it is induced by falling temperature whilst it raises the viscosity and lowers the conductivity.

Since the last communication from this laboratory, measurements of the conductivity of sodium and potassium oleates by Dennhardt (*Diss.*, Erlangen, through Ubbelohde and Goldschmidt, "Handbuch der Chemie und Technologie der Oele und Fette," Vol. III) have come to our notice. Dennhardt also observed a slight displacement of the minimum in the sodium oleate curves toward more concentrated solution with falling temperature. On the other hand, his temperature-coefficient varied by 40 per cent., being at a minimum in $N/10$-solution. His results may, however, be placed out of court, since his conductivity results are only half as great as those of Kahlenberg and Schreiner (*Zeitsch. physikal. Chem.*, 1898, **27**, 552). Equally untenable is his hypothesis of the existence of an emulsion of free oleic acid in alkaline solution and his assumption that the replacement of a salt by sodium hydroxide would cause a falling off in conductivity and explain the observed minima.

The most important feature of the present temperature-coefficients is their high value. This is brought out when we compare the ratios of the specific conductivities at 90° and 50° for typical classes of electrolytes. The value for nitric acid is interpolated from data in the literature, the other three values were directly determined for this purpose; the coefficients refer to $N/20$-solutions. The value for nitric acid is 1·36, that for sodium hydroxide 1·473, that for sodium acetate 1·656, whilst that for sodium myristate is no less than 1·862. The abnormally high value for soap would appear to be due to probable increase of hydrolysis on heating, accompanied by diminished adsorption of alkali by the colloidal matter.

The essential uniformity of the effect of temperature on the conductivity over so very large a range of concentrations would tempt one to the conclusion that, therefore, the degree of dissociation was independent of the temperature. This may indeed be the case, even although, of course, the temperature-coefficient of μ_{∞}, the conductivity at infinite dilution, must possess a normal value. The conclusion which may be drawn is that temperature affects the hydrolytic equilibria of all concentrations much in the same way, and not, as one might have expected, in relation to the absolute concentration of the alkali formed.

Conductivity at Room Temperature.[*]

$N/20$-Sodium myristate can be kept for about half an hour at 25·0° before it solidifies. Solidification takes place from numerous points throughout the liquid; it occurs very rapidly when it once sets in, the change taking only two or three minutes. The molar conductivity of $N/20$-solution at 25·0° (after it has been at 25·0° for about twenty minutes brought from 90·0° in a silver tube) varies from 34·2 to 35·1 mhos. On solidification the conductivity is halved, being about 16 to 17 mhos; this value further diminishes during the course of the next two hours by a fraction of 1 mho.

In the case of $N/5$-solution, which alters only slowly after the second minute, the conductivity becomes appreciably constant between the fourth and sixth minute, but between the seventh and tenth minute it increases about five-fold, solidification, of course, taking place. The conductivity at the end of an hour has become constant, as it only decreases 1 or 2 per cent. in the course of a further sixteen hours. The values for the molar conductivity are 34 mhos at five minutes while liquid; 6·3 mhos at one hour; 6·1 mhos at seventeen hours. Presumably the much greater effect of solidification in this concentration as compared with $N/20$-solution is due to the much greater mechanical resistance resulting from solidification. Kahlenberg and Schreiner (*loc. cit.*) found at 25° an increase of ten-fold in the resistance of a $N/8$-potassium stearate solution on solidification.

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[*] Allowing the myristate solutions, or, at least, the more dilute ones, to solidify without removing the electrode, does not break the glass, as happens with the palmitate.

A *N*/2-solution of sodium myristate was measured in the solid state; at the end of half an hour at 25° it had a value of about 8 mhos.

*Appearance and Behaviour of Sodium Myristate and Laurate Solutions.**

Sodium Myristate.

	1·5*N*	1·0*N*	0·8*N*	0·5*N*	0·2*N*	0·1*N*	0·05*N*	0·01*N*
90°...	vis.; not op.	f. fl.; not op.	fl.; not op.	fl.; not op.	v. fl.; not op.	v. fl.; not op.	v. fl.; sl. op.	v. fl; sl. op.
60°...	vis.; not op.	tr.; gr. susp.	f. fl.; tr.; gr. susp.	—	fl.; op.	—	—	—
50°...	white solid	v. vis.: tr.; gr. susp.	sl. vis.; tr.; cell.	fl.; gr. susp.	—	—	—	—

v. = viscous; sl. = slightly; v. = very; f. = fairly; fl. = fluid; op. = opalescent; not op. = absolutely clear and transparent; tr. = transparent, that is, not milky; gr. susp. = granular suspension; cell. = suspension of obvious cellular structure.

The appearance at 40° or 50° depends on whether the solution has previously been at a higher or lower temperature; thus a 0·5*N*-solution at 50° cooled from 90° is as shown in the table, but if it has been raised from room temperature it contains remains of a cellular structure, the translucent network floating near the bottom of the solution and being so soft that bubbles readily rise through it. At room temperature 0·01*N*- and ("undercooled") 0·05*N*-solutions of myristate are partly coagulated; white, jelly-like masses separate out and leave a clear liquid.

It is an important fact that "supersaturation" or "undercooling" of the gelatinisation may readily occur; thus a 0·2*N*-sodium laurate solution which has been liquid for days at room temperature at once turns solid on jarring, or scratching the side of the bottle. A 0·1*N*-sodium laurate solution which has been mostly liquid for months "sets" in a few hours after being jarred and shaken. It will be noticed that these periods are much longer than those discussed in connexion with the conductivity measurements at 40° and 50°. There is no room left for doubt that gelatinisation is not identical in kind with the process of attainment of equilibrium within the liquid sol. The latter may have ceased to alter in conductivity, and McBain and Taylor (*loc. cit.*) have shown that a true reversible equilibrium is attained from both sides at least at higher temperatures, whilst the sol is "supersaturated" with respect to gelatinisation. This would appear to show that the gelatinisation

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* Compare McBain and Taylor (*loc. cit.*) for palmitates.

is not a process continuous with the adjustment of the degree of dispersion of a colloid. S. Odén (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 100) found that coagulation and "redissolving" colloidal sulphur in dilute sols did not affect the diameter of the sulphur particles, thus showing the analogous behaviour of suspensoid colloids.

The distinctive appearance of 0·5*N*-sodium laurate at room temperature is worthy of mention. This solution (solid) after a day at room temperature (in a Jena-glass bottle with glass stopper heavily smeared with vaselin, as usual) develops a striking and beautiful lustrous surface against the glass, like white satin or even like a polished piece of white metal. 0·2*N*-Sodium laurate is the only other soap that we have observed to possess this property at all.

The "melting" points of the sodium myristate solutions when the temperature is raised about 1° in ten minutes are as follows, if we take as "melting point" the temperature at which the solid loses its hold of the inner surface of a Jena-glass bottle. Even the 0·05, 0·1, and 0·2*N*-jellies show no tendency to form a level surface when tilted, until a temperature 1·5° higher has been attained. Soon after, say, at 2° above the temperature tabulated, much liquid is formed, but at this rate of heating the solid white jelly does not wholly disappear until 4·0° above the temperatures given in each case.

1·0*N*	0·5*N*	0·2*N*	0·1*N*	0·05*N*	0·01*N*
51·7°	50·2°	46·4°	41·5°	41·0°	(compare p. 2054)

These "melting points" are, of course, very ill-defined,* and they bear but little relationship to Krafft's so-called "temperature of crystallisation" (*Ber.*, 1895, **28**, 2566; 1899, **32**, 1596) in the dilute solutions. In the more concentrated solutions, however, they must, apart from undercooling effects, be nearly identical with these. Krafft obtained for 0·8*N*-sodium myristate 52° to 53°, but for 0·04*N* 31·5°; the latter solution must have been quite appreciably undercooled. Our results show a marked similarity of melting temperature over a fairly wide range. There seems to be no explanation as yet for the fact that the melting points of all pure solutions of sodium soaps melt a little below the melting point of the corresponding acid (1·5*N*-sodium laurate melts at 42°, lauric acid at 42·9°). Goldschmidt (Ubbelohde and Goldschmidt, "Hand-

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* Thus, a 0·5*N*-solution kept for many hours at 40° (from room temperature) consists of white flocks, touching, and forming, say, 9/10ths of the solution, suspended in a colourless coagulum. Sometimes this solution would flow (0·5 cm. per minute under 15 cm. head through a hole 3 mm. in diameter).

buch der Chemie und Technologie der Oele und Fette," p. 412—414) attempts to explain Krafft's results by assuming that the solid "crystallising" out is a solid solution of neutral soap in fatty acid. A glance at the quantitative data of Donnan and White (Trans., 1911, **99**, 1675) serves to exhibit the inadequacy of this explanation.

Summary of Results.

The anomalous conductivity-curve for sodium palmitate at 90° is closely paralleled by that of the very much more mobile myristate solutions. The laurate curve is much less anomalous in that the maximum and minimum are obliterated. Only the degree, and not the position, of the abnormality in the curves is altered in passing down the homologous series from stearate to laurate. The conductivity curves of sodium myristate at a number of temperatures between 90° and 40° reveal a very high temperature-coefficient which, however, is nearly uniform for all concentrations, so that the position and degree of development of maximum and minimum is largely unaffected. Finally, a number of qualitative observations closely bearing on the colloid theory of soap solutions and "supersaturation" of gelatinisation have been discussed. The coagulation of a suspensoid or gelatinisation of an emulsoid does not appear to be connected with change in the degree of dispersion of the colloid in certain cases.

In conclusion, we desire to take this opportunity of expressing our thanks to the Research Fund Committee of the Chemical Society, and to the Colston Society of the University of Bristol, for grants towards the purchase of materials and apparatus.

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The University, Bristol.

CCXVI.—*The Wet Oxidation of Metals. Part II. The Rusting of Iron* (continued).

By Bertram Lambert.

The supporters of the acid theory of the rusting of iron claim that the dominant factor in the atmospheric corrosion of the metal is carbonic acid, and the assertion is made that iron—by which is meant commercial forms of the metal—will not rust when placed in contact with water and air (or oxygen) free from all traces of carbonic acid. The experiments cited in favour of this argument are those of Moody (Trans., 1906, **89**, 720) and of Friend (*J. Iron Steel Inst.*, 1908, II, 16; Proc., 1910, **26**, 179; "The Corrosion of Iron and Steel," p. 57). Both these experimenters succeeded in keeping commercial iron free from rust in contact with water and air, from which the acid constituents had been removed, but it was only after the metal had been treated in the one case with chromic acid solution and in the other case with a solution of sodium hydroxide. It has recently been proved (Dunstan and Hill, Trans., 1911, **99**, 1853) beyond any doubt that the treatment of iron with these reagents alters the character of the surface of the metal in such a way as to make it what is called passive. Now iron in this passive condition can be kept without rusting in contact with water and air free from all traces of carbonic acid (or other acids), but if ordinary air containing carbonic acid is substituted for the purified air, rusting readily takes place, as the experiments of Moody and of Friend have shown. It is now known (Dunstan and Hill, *loc. cit.*) that carbonic acid readily destroys the passive condition of the iron, and so the substitution of ordinary air for purified air in these experiments really involved two changes in the conditions of the experiments, namely, a change in the atmosphere and a change in the iron. It is illogical to attribute the corrosion of the iron to one of these changes and to ignore the influence of the other change. Neither of the experimenters ever succeeded in keeping ordinary "untreated" forms of commercial iron free from rust in contact with water and purified air.

It may be said, then, that the experiments of Moody and of Friend prove only that passive iron may be kept free from corrosion in contact with water and air in the absence of acid constituents; but these conclusions are not necessarily applicable to ordinary "untreated" forms of commercial iron or to pure iron. There is thus lacking any real experimental foundation for the acid theory of corrosion.

Much experimental work has been done in recent years with the object of proving that commercial forms of iron will always undergo corrosion when placed in contact with water and oxygen, even in the absence of carbon dioxide or other acids. The supporters of the acid theory of corrosion criticise most of this work on the ground that sufficient care has not been taken to remove all traces of carbonic acid from the various forms of apparatus used (Friend, "The Corrosion of Iron and Steel," p. 44–67; H. E. A., *Science Progress*, 1911, **22**, 642). This criticism, along with others which are considered later, has been applied to the experiments performed by the author and Mr. Thomson (Lambert and Thomson, Trans., 1910, **97**, 2426).

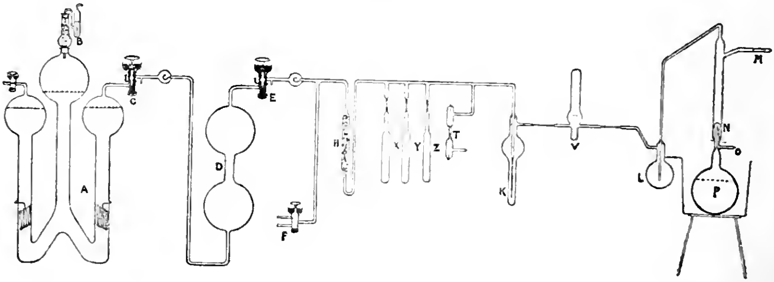
The experiments have been repeated with the utmost care and with additional refinements and precautions. The results go to show that none of the criticisms is valid, and that the claim which is founded on the experiments is substantially accurate, namely, that commercial forms of iron will undergo corrosion quite readily in contact with pure water and pure oxygen, under conditions such that carbonic acid (or any other acid) can neither be present nor be formed during the reaction.

The following is a full account of a final experiment in which all the precautions and refinements suggested by previous experience are included. The criticisms of the original experiments are dealt with in the course of this description.

The Preparation of the Oxygen.

The oxygen was prepared by the electrolysis of a solution of barium hydroxide in conductivity water. The barium hydroxide was crystallised many times even after careful tests had failed to show any impurities, and the crystals were separated from the mother liquor after each crystallisation by means of a centrifuge. A saturated solution of the barium hydroxide was electrolysed between platinum electrodes in a cell, *A* (Fig. 1), and the air entering the reservoir of the cell owing to changes of pressure during the electrolysis was purified by passing through tubes containing sulphuric acid and soda-lime, as shown in the figure at *B*.

Fig. 1.



The oxygen was stored in the flasks *D* of about 2 litres capacity. The taps *C* and *E* separating the electrolytic cell from the storage vessels, and the latter from the rest of the apparatus, were large Schmidt mercury taps, and were lubricated with glacial phosphoric acid. These taps, which have a device for filling the bore of the tap with mercury, were found to be very satisfactory, and entirely prevented any leak round the barrel, even when a wet gas was kept on one side of the tap and the highest vacuum on the other side for a period of several weeks.*

Preparation of the Water.

The water was prepared by distillation under diminished pressure from a solution of barium hydroxide in conductivity water. The barium hydroxide, purified as before, was dissolved in conductivity water in the flask *P*, which was separated from the rest of the apparatus by a thin bulb, *N*, sealed into a wider tube connected with the apparatus as shown in the figure. Connexion was made between the water reservoir and the apparatus at the proper time (see later) by causing the heavy glass rod at *M* to drop on the thin bulb and break it. The air in contact with barium hydroxide solution was removed through the side-tube *O*, which was drawn out and attached to a good water-pump. The water in the flask was then boiled vigorously under diminished pressure for two hours, and the capillary sealed whilst the water was boiling. In this way all but the smallest traces of air were removed from the flask.

Friend (*loc. cit.*) has asserted, without adducing any experimental proof, that "barium hydroxide is not sufficiently powerful to remove every trace of carbon dioxide from the air contained in a flask with a saturated solution of the base"—that "its aqueous solution is in equilibrium with a definite, although minute, partial pressure of carbon dioxide." He puts this forward as a serious objection to the work done by the author and by other experimenters who have prepared the water used in their work on this subject by distillation from a solution of barium hydroxide. The spectroscopic examination of the water-vapour in contact with the barium hydroxide used in these experiments has shown that Friend's assertion has no foundation in fact. Fig. 2 shows the apparatus which was used for the spectroscopic examination of the water-

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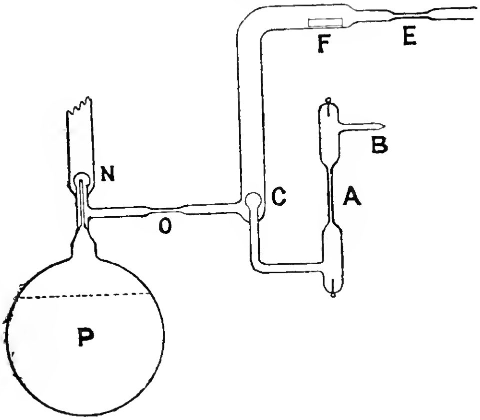
* When a glass tap has been well ground and is mercury-sealed there is no danger of any leak from the outside, provided that the lubrication with glacial phosphoric acid has been carefully done, but even the best taps when lubricated with glacial phosphoric acid will not prevent a leakage round the barrel of the tap, if it is used to connect vessels containing a wet gas with vessels in which a high vacuum is to be maintained for any considerable length of time, unless the bore of the tap is filled with mercury. In earlier experiments much trouble was experienced on this account (*loc. cit.*, p. 2426), and a special trap device was used to cope with the difficulty; further, the oxygen was passed through a tube containing pure sodium hydroxide to remove excess of moisture and so minimise the risk of leakage. The use of Schmidt taps has done away with the necessity for these devices. The production of a high vacuum in the storage vessels, when the sodium hydroxide tube was used, was a long and tedious operation, and the heating of the vessels to remove surface films of gases could not be done very satisfactorily.

vapour and traces of residual air in contact with the barium hydroxide solution. A Plücker tube, *A*, with platinum electrodes was connected with the flask *P*, as shown in the figure, being separated by means of a thin glass bulb, *C*, which could be broken at the proper time by means of the heavy glass rod, *F*. The Plücker tube was first exhausted thoroughly through the side-tube *B*, which was then sealed off; the exhaustion was carried to the point when no discharge could be made to pass between the platinum electrodes, even when the tube was strongly heated with a Bunsen burner. A good water-pump was attached beyond *E*, and the barium hydroxide solution in *P* was boiled vigorously under diminished pressure for two hours. The capillary at *E* was sealed off while the boiling was in progress. The flask *P* was then cooled until all the liquid water had been condensed back into it. Finally, the bulb *C* was broken by means of the glass rod *F*, and the water-vapour and any residual air was allowed to enter the exhausted Plücker tube. A discharge was passed through the tube by means of a large coil, and the spectrum of the discharge examined. There was no trace of the carbon dioxide spectrum under any conditions; in fact, a remarkably pure water-vapour spectrum was obtained.*

FIG. 2.



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* In some trial experiments, the spectrum also contained some weak nitrogen bands, but in these cases there was a blank end in the apparatus and the air could not be completely swept out by the steam. Some similar experiments were done with barium hydroxide solution, containing considerable quantities of barium carbonate, but no trace of the carbon dioxide spectrum was ever discovered in the discharge.

The Choice of Vessel for the Reaction.

The choice of the kind of vessel in which the iron was to be brought in contact with the water and oxygen was only made as the result of a long and careful series of experiments.

It was finally decided to use vessels made of transparent fused silica * as being least likely to be affected by either water, iron, or oxygen. A simple form of glass vessel was devised, which with a tube of clear fused silica gave all the advantages of an apparatus made entirely of silica, since the water which collected in the silica tube and came in contact with the iron must have condensed only on the inside of the silica tube itself. The silica tubes were about 8 cm. in length and 1 cm. in diameter, and were sealed at one end.

A silica tube was made to slide loosely into an outer glass vessel, of the shape shown at *V* in the figure, and was so supported by the lower end of the glass vessel that the open end of the tube and half its length were not in contact with the glass. The iron was put into the silica tube, which was then placed in the outer glass vessel; the glass vessel was then closed at the top, and sealed into position by means of the side-tubes connected with the oxygen supply and the water supply, as shown in the figure. These side-tubes were drawn out to capillaries in order to facilitate the sealing off of the vessel when the experiment was finished. (Three or four such vessels were used in each experiment, and were sealed on in parallel.)

Between the vessel *V* and the water reservoir *P* was a trap *L*

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* An objection (T. M. L., *Nature*, 1911, **86**, p. 25 ; Friend, *loc. cit.*) has been raised to the use of quartz vessels on the ground that the fused silica dissolves in water to form silicic acid, and that this acid might be quite sufficient to dissolve the iron and thus play a similar part to that which has been attributed to carbonic acid in the atmospheric corrosion of iron. This possibility had been considered, but, as the result of a long series of experiments lasting several months, the danger was held to be negligible.

In these experiments, commercial iron was brought in contact with pure water and pure oxygen under exactly the same conditions in (*a*) fused quartz vessels, (*b*) fused quartz vessels lined with purified paraffin wax, (*c*) Jena-glass vessels lined with purified paraffin wax.

In all cases, the water which came in contact with the metal could only have condensed on the inside of the vessel containing the metal. The paraffin wax used to line the tubes had been purified by long continued extraction with boiling conductivity water. The results were exactly the same in all the experiments.

Rusting was visible in all cases within a few hours. The iron rusted in spots as it always does, and rusting did not first take place at the points where the metal touched the sides of the containing vessels. The objection to the use of quartz vessels cannot then be considered valid, and it is obvious that quartz vessels have enormous advantages over vessels of any other material. The solubility of the quartz is, in any case, exceedingly small (much smaller than that of any kind of glass), and the vessels lend themselves admirably to cleaning and purification.

to catch and retain any water which was condensed before reaching this point. Between the vessel *V* and the oxygen supply was a trap *K* of the shape shown in the figure. The first fractions of water which were distilled from *P* during the actual course of the experiment were caused to condense in this trap by surrounding it with ice. This water was used for washing the oxygen on its way from the storage vessel to the tube *V* (see later). Three bulbs, *X*, *Y*, and *Z*, were sealed on to the apparatus as shown. At three separate stages of the experiment one of these bulbs was cooled in liquid air, whilst the rest of the apparatus was heated, and then the bulb, whilst still immersed in the liquid air, was sealed off at the capillary (see later). The Plücker tube, *T*, with platinum electrodes, was used for the spectroscopic examination of residual gases during the last stages of the exhaustion. The tube *H* containing glass beads * covered with gold-leaf was used to protect the vessel containing the iron from contamination with mercury-vapour, for very high vacua were obtained and sometimes retained over long periods.

All the joints in the apparatus were sealed glass, and no rubber connexions of any kind were used. All the glass parts of the apparatus were most carefully cleaned and steamed for long periods. The final sealing together of the various parts was done after the room had been closed for several days, and the air which had to be blown into the apparatus during the process of sealing was passed through a tube containing soda-lime.

The silica tubes were boiled with pure concentrated nitric acid for several weeks, and were afterwards steamed and boiled with constant changes of conductivity water for some days. They were finally heated strongly in a clear blow-pipe flame.

The whole apparatus was connected, through the tap **F**, to an automatic Sprengel pump and a large drying tube containing phosphoric oxide.

Method of Conducting the Experiment.

The bore of the Schmidt tap *C* was filled with mercury, and then the whole apparatus between this tap and the bulb *X* was thoroughly exhausted. During the last stages of the exhaustion the apparatus was strongly heated. Between *H* and *L* this heating was very effectively done by heating a large metal plate fixed under

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* In earlier experiments, small plugs of glass wool were used to keep the glass beads in position, but it was found that glass wool gave off carbon dioxide on heating in a vacuum, even after it had been carefully washed and steamed, so that its use was abandoned. Jena boro-silicate glass, broken into small pieces and subjected to careful washing and steaming, was used and found to be very satisfactory.

the apparatus, with a hood of sheet asbestos covering the parts above it. The oxygen storage vessels and other parts, which could not be heated thus, were heated by means of a large blow-pipe flame. Before the heating was begun all the outer surface of the glass was covered with a thin layer of soot so as to lessen the risk of fracture.

The vacuum was examined by means of the discharge produced by a large coil in the Plücker tube *T*. During the last stages of this first exhaustion, whilst the glass surfaces were being heated, the spectrum of carbon dioxide was seen, but it disappeared after some time and the heating and exhaustion were continued until no discharge could be made to pass in the Plücker tube. The tap *E* was then closed, and the storage vessels filled with oxygen, which was afterwards allowed to enter the apparatus. Then the apparatus and storage vessels were again exhausted and thoroughly heated until no discharge would pass in the Plücker tube. During the last stages of heating and exhaustion the bulb *X* was immersed in liquid air and sealed off whilst still in the liquid-air bath.

The apparatus was then tested by allowing it to remain for ten days, and the vacuum was examined as before. No discharge could be obtained until the whole apparatus had been strongly heated, and even then the discharge in the Plücker tube was only an occasional, faint, fluorescent flicker, and no spectrum could be obtained.

The apparatus was then twice washed out with oxygen, and the whole, including the oxygen storage vessels, exhausted, and heated after each filling with oxygen. During the last stages of the second exhaustion the bulb *Y* was immersed in liquid air for a period of two hours whilst the apparatus was heated, and was then sealed off whilst still immersed in the liquid air.

The operations of washing out with oxygen, exhausting, and heating were then repeated four times, the exhaustion being carried on each occasion beyond the point when no discharge could be obtained in the Plücker tube. Finally, the bulb *Z* was immersed in liquid air whilst the rest of the apparatus was heated for four hours, the bulb being sealed off whilst in the liquid air.

The whole apparatus was thus exhausted eight times beyond the stage when no discharge could be obtained in the Plücker tube; it was washed out with oxygen seven times, and the residual gases were frozen out at three separate times with liquid air. The experiment lasted nearly five weeks.

This elaborate treatment was carried out in order to test the validity of the criticisms which have been made of former experiments on the ground that carbon dioxide had not been removed from the apparatus used. It is very significant that after the air had been removed from the apparatus and the first heating completed, the carbon dioxide spectrum was never again seen.

The next step was to put the apparatus in connexion with the water reservoir by breaking the thin bulb *N* by causing the glass rod at *M* to fall on it.

The flask *P* was then very gently heated on a water-bath, the temperature never being raised so high as to promote rapid evaporation. The first portions of water distilled from *P* were made to condense in the vessel *K* by surrounding it with ice. When the water in *K* had reached a depth of about 12 cm., the lower end of the vessel *V* was cooled, and water slowly condensed inside the silica tube and in contact with the iron. This water must necessarily have condensed on a quartz surface; any water condensed on the walls of the glass vessel supporting the silica tube simply ran down and collected outside the silica tube.

When a sufficient quantity of water had been obtained in contact with the iron, the capillary to the right of *V* was sealed off by means of a small flame. Oxygen which had meanwhile been made and stored in *D* was then allowed to enter the apparatus by opening the tap *E*. This pure oxygen, before coming into the vessel containing the iron, was washed by passing through the pure water collected in the trap *K* for this purpose. The capillary to the left of *V* was then sealed, thus leaving the iron in contact with pure oxygen in a sealed vessel.

In this experiment three similar vessels, *V*, were used, and sealed on in parallel.

Three different kinds of commercial iron were used, one in each vessel, namely, (1) a pure commercial electrolytic sheet iron, (2) Kahlbaum's pure iron foil, and (3) a cylinder of iron turned from a large nail taken from the roof of Merton College library while repairs were being carried out. This nail was made of very soft iron, and was more than two hundred years old.

The iron in each case was carefully polished with fine carborundum and then with Swedish filter paper. The results in all three cases were the same, and did not differ in any respect from the results obtained with other good specimens of commercial iron used in earlier experiments. Corrosion was visible in a few hours, and a considerable quantity of rust had formed within a few days.

Corrosion thus took place in all these three commercial varieties of iron when placed in contact with pure water and pure oxygen in vessels which had been proved to have no influence on the reaction. The water-vapour had been tested spectroscopically, and the oxygen also had been subjected to very thorough spectroscopic examination.

The glass walls of all the vessels with which the water and oxygen came in contact had been subjected to the exhaustive treatment described above, and so it may be said to be proved beyond any reasonable doubt that oxygen and water—both of the highest obtainable purity—have the power, of themselves, of causing commercial iron to rust.*

Further, the rusting seemed to take place as quickly as it does in ordinary air or oxygen, and so it cannot any longer be maintained that carbon dioxide or any other acid is the "dominant factor in the atmospheric corrosion of iron," where commercial forms of the metal are meant.

An Electrolytic Theory of the Corrosion of Iron.†

It is well known that whilst ordinary commercial impure zinc readily dissolves when placed in dilute sulphuric acid, the pure metal is scarcely affected unless metallic connexion is made between it and another more electronegative metal, either within or without the liquid. Under these conditions the pure zinc dissolves, but the action ceases immediately the metallic contact between the pure zinc and the more electronegative element is broken.

In impure zinc the more electronegative element is already present, within the mass of metal, in the form of minute impurities, such as copper or lead or perhaps as another form of the metal which is relatively electronegative to the main mass of the metal.

Whenever we have two metals (or two modifications of the same metal) which are electrically different, that is, have different solution-pressures, and they are placed on metallic contact in an electrolyte, then the relatively electropositive part will dissolve with the production of an electric current flowing through the electro-

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* There is a possibility that, under the combined influence of water and oxygen, the carbonaceous impurities in the commercial iron may be oxidised, producing carbon dioxide. This has been shown not to be the case by a very careful and exhaustive spectroscopic examination of the oxygen and water-vapour which had been in contact with one of the specimens of iron for a period of nine months. No trace of the carbon dioxide spectrum could be obtained under any conditions.

† Electrolytic theories of the corrosion of iron have been discussed by Whitney (*J. Amer. Chem. Soc.*, 1903, **25**, 394), Tilden (Trans., 1908, **93**, 1356), "H. E. A." (*Science Progress*, 1911, **22**, 311), and others; but the writers discuss the question from different points of view, and, in consequence, much confusion and misunderstanding has arisen as to the interpretation of the so-called "electrolytic theory." I have stated here my own interpretation of the theory, which we owe, in the first place, to Faraday.

lyte from the electropositive to the electronegative pole, and in the opposite direction through the metal.

The rate of such a reaction depends: (*a*) on the magnitude of the difference of electric potential, that is, the difference of solution-pressure, between the two metals or the two modifications of the same metal, and (*b*) on the resistance offered by the electrolyte to the passage of the electric current.

No part of the metal can dissolve unless an electric current actually passes through the electrolyte. The rate of the reaction may, however, be so infinitesimal that the amount of metal passing into solution will not be sufficient to respond to chemical tests even after long periods.

Let us consider, in this light, the case of a piece of ordinary commercial iron in contact with the electrolyte water.

Such a piece of iron is impure and not homogeneous—there are some parts of it which have a different solution-pressure from other parts—and so, when it is placed in contact with the electrolyte water we have all the conditions for the production of an electric current.

If the conditions are such that an appreciable electric current can pass between the two electrically different parts of the iron, the metal will dissolve at the relatively electropositive parts. The fact that iron is practically insoluble in pure water (in the absence of oxygen) shows that the current which actually does pass is so infinitesimal that the amount of iron dissolved cannot be detected, even after long periods, by chemical means.

This may be due to two causes, namely, (*a*) the small magnitude of the electromotive force owing to the small differences of potential between the electrically different parts of the metal, and (*b*) the great resistance offered to the passage of an electric current by the electrolyte.

It has been shown earlier that commercial iron rusts when placed in contact with water and oxygen of the highest obtainable purity, and that the rate of the corrosion is almost the same as when ordinary distilled water and oxygen (or air freed from acid constituents) is used. It is generally accepted that iron must pass through a process of solution before rust is produced, and so, whilst the metal is practically insoluble in pure water alone, it must be soluble in the presence of oxygen. It follows, then, that oxygen must bring about some alteration in the conditions of the "voltaic circle"—commercial iron and water—in such a way that a greatly increased electric current passes between the electrically different parts of the iron. That oxygen can bring about such a change of conditions is beautifully illustrated by an experiment described by

Dunstan and Hill (*loc. cit.*). Cushman (*Amer. Soc. Testing Materials*, 1907) has shown that if a piece of commercial iron is left in contact with a solution of sodium chloride to which a little phenolphthalein has been added, a pink colour develops in the solution which is in contact with some parts of the metal. These colour zones are always confined to a portion (or portions) only of the metal, and indicate the presence of hydroxyl ions (or free alkali) at these points. After being kept some time, the metal beneath the pink zones remains quite bright, but corrosion takes place gradually at the other parts of the metallic surface. This experiment shows that the solution is being electrolysed, and that iron is passing into solution at those parts not marked out by the pink colour of the phenolphthalein. It shows also that some parts of the iron are electrically different from other parts, and that the electromotive force produced by these differences of solution-pressure is enough, under these conditions, to cause the passage of an electric current of sufficient magnitude to produce perceptible electrolysis of the solution of sodium chloride.

It was shown by Dunstan and Hill, however, that the extent of this electrolysis was conditioned by the presence of oxygen, because, in the absence of air (or oxygen) the pink zones were not developed, and therefore an electric current sufficient to produce perceptible electrolysis could not pass.

Oxygen, therefore, must do one of two things—it must in some way or other increase the electrical differences between the parts of the metal and so increase the electromotive force, or it must reduce the resistance of the circuit. We have no real experimental evidence of the truth of either of these alternatives, but it has been generally assumed hitherto that oxygen acts by diminishing polarisation.

It will be seen that the validity of a theory based on differences of solution-pressure between different parts of the metal is not affected by the question whether iron is soluble to any appreciable extent in water in a vacuum. It is sufficient that there should be a tendency for the iron to dissolve.

If it be granted that pure water is an electrolyte and that ordinary commercial iron is not homogeneous, then it must follow that such iron tends to dissolve, in parts, with the electrolysis of the water.

It seems certain from what has been said above that oxygen has the power, in some way not yet clearly understood, of greatly increasing the rate of this electrolysis, and consequently greatly increasing the rate at which the iron passes into solution.

If, however, differences of solution-pressure exist, however minute they may be, in a piece of iron, the final concentration of the dissolved iron must eventually be the same, although the time taken to reach this equilibrium may be very great.

The study of the properties of the pure iron prepared by the author adds some confirmatory evidence of the validity of the above considerations, but it will be seen that there are many difficulties still in the way of accepting any simple theory of the corrosion of iron until more experimental facts are available.

The Properties of Pure Iron.

Behaviour towards Water and Oxygen.—Pure iron has been kept in contact with pure water and pure oxygen, under atmospheric pressure, for more than two years without showing any signs of corrosion or alteration of any kind. Further, ordinary air can be substituted for pure oxygen and ordinary tap-water for pure water, and the result is the same—the surface of the metal remains bright and untarnished for an apparently indefinite time. The explanation of this fact is to be sought in the greater homogeneity of the iron, due to its purity. If such iron be really homogeneous, and all parts of it have the same solution-pressure, then, on the above theory, a piece of metal placed in contact with an electrolyte will not furnish the conditions for the production of an electric current; since there is nothing to bring about the passage of an electric current, the iron cannot therefore pass into solution and no corrosion can take place. It does not necessarily follow from the fact that the iron does not rust that there must be perfect homogeneity in the metal. It may be that differences of electric potential do exist on the surface of the iron, but they are so much smaller in this iron than in any commercial varieties of the metal that, in the presence of water and oxygen, the electric current which passes between the points of different solution-pressure is so small that the amount of iron passing into solution is not sufficient for the formation of a perceptible amount of rust even after long periods.

A striking confirmation of the truth of this argument is afforded by the following experiment: Some pieces of pure iron which had been exposed to water and air for several months without showing any signs of corrosion were carefully dried between Swedish filter papers. Some of the pieces were then placed in a polished agate mortar and pressed strongly with an agate pestle, whilst others were left untouched. All of them were then again put in contact with water in silica tubes and exposed to the air. The pieces which had been subjected to pressure in the agate mortar showed signs of corrosion in less than an hour, and after several hours a golden-yellow deposit of rust had formed on those parts of the iron which had not been pressed, whilst the parts which had been pressed by actual contact with the agate remained quite bright. Those pieces of iron which had not been pressed showed no signs of corrosion, proving that the process of drying had not been the cause of the striking alteration in property of the pieces which had been put under a strain.

The pieces of metal which had been subjected to pressure consisted of two modifications of iron, a pressed part and an unpressed part. These two varieties of iron would have a different solution-pressure, and so, when placed in contact with the electrolyte water, would constitute a self-contained galvanic element. The fact that rust formed on the unpressed part showed that iron passed into solution at that part, which was therefore relatively electropositive to the pressed part.

That the pure iron is not absolutely homogeneous—that it does possess electrically different parts—is indicated by its behaviour towards acids and towards solutions of salts of the alkali metals in the presence of air or oxygen. These reactions are still under investigation, and can only be considered very briefly at present.

It may be said generally that cold dilute sulphuric and nitric acids have very little visible action on the metal, but that even very dilute cold hydrochloric acid causes the slow evolution of bubbles of hydrogen. The metal readily dissolves in all three acids on warming, but, again, hydrochloric acid is much more vigorous in its action than the others.

The action of solutions of alkali salts on the metal in contact with air shows many irregularities which still await investigation. Pure iron which had been exposed to the action of water and air for many months without showing any signs of rusting, underwent corrosion in a few hours when transferred to a normal solution of sodium chloride in air.

That other constituents of the air besides oxygen play no part in this reaction is shown by the fact that corrosion took place just as readily when pure oxygen was used.

The chlorides of potassium and ammonium seem to have a similar action, but, curiously, the corresponding sulphates and nitrates behave differently. The pure iron may be exposed to concentrated solutions of the sulphates and nitrates of sodium, potassium, and ammonium in the presence of air, often for many days, without undergoing much corrosion.

It seems quite possible that the study of the action of salt solutions on pure iron may bring to light some definite evidence for the view held by the author that a considerable factor in determining the corrosion of commercial iron is the alteration in the electrical character of the different parts of the metal brought about by the action of salts and acids.

The Behaviour of Pure Iron towards Solutions of Copper Salts.—It is well known that all ordinary forms of iron, when placed in contact with solutions of copper salts, are immediately covered with a deposit of metallic copper. It is only when the metal has been rendered "passive," by one of the many processes which produce this condition, that iron can be made to remain unaffected in a solution of a copper salt. The copper salt solution must be very dilute, and even then the passive iron recovers its ordinary behaviour after several hours, and causes copper to be deposited on it.

Pure iron will withstand the action of a saturated solution of copper sulphate or copper nitrate, at the ordinary temperature, for an apparently indefinite time, without losing any of its metallic lustre and without any perceptible trace of copper being deposited.

Some specimens of iron which had been exposed for several months to a concentrated solution of copper sulphate were removed, washed, and dried, and examined under the microscope. The curious structure of the surface was exactly the same as it was before the iron was placed in contact with the copper sulphate solution.

Pure copper sulphate, free from iron, was used, and the solution after being in contact with the iron for many months failed to give any test for the presence of iron.

If the temperature of the copper sulphate solution is raised to that of boiling water, deposition of copper on the iron slowly occurs, and finally, after some hours, the iron passes into solution completely, and copper is left behind in the form of very small crystals.

Copper is also deposited on the iron if it is pressed in an agate mortar before being put in the solution of copper sulphate, or if it is pressed with a quartz rod while under the copper sulphate solution.

The behaviour of the pure iron towards copper chloride is, however, quite different. If a concentrated solution of copper chloride is used, the iron becomes coated with copper immediately it is put into the solution, and, within a few minutes, the iron all disappears, and only finely divided copper remains.

If a very dilute solution (less than 1 per cent.) of copper chloride is used, the action is slower. For a few seconds the iron retains its brightness; then dull spots are seen at some points on the surface of the metal; these quickly spread over the whole surface of the iron, and the reaction proceeds to an end, as before, in a remarkably short space of time.

The experiment is perhaps even more striking if carried out in a vacuum. The finely divided copper, which is left after the first reaction, slowly dissolves, and finally white, insoluble cuprous chloride is left.

Similar results are obtained if a solution of sodium chloride is added to solutions of the sulphate and nitrate of copper.

Ordinary metallic aluminium behaves in much the same way towards solutions of copper salts. The metal is not affected by solutions of copper sulphate or copper nitrate, but, if copper chloride is used, or if sodium chloride is added to the solutions of copper sulphate or nitrate, precipitation of copper on the aluminium immediately follows.

This behaviour of aluminium has been attributed to the fact that the metal, under many conditions, becomes coated with a protective film of hydroxide or basic salt.

It is assumed that this protective film is more readily soluble in the hydrochloric acid produced by the hydrolysis of the copper chloride than in the sulphuric or nitric acids from the sulphate or nitrate respectively. This argument is strengthened by the fact that aluminium is readily dissolved by hydrochloric acid, whilst it is practically unaffected by sulphuric or nitric acids even at 100°.

Experiments have shown that the same arguments cannot possibly hold good in the case of pure iron.

It is very improbable that iron prepared by the reduction of the oxide by hydrogen at a high temperature, and allowed to cool in the gas, would have a film of oxide on the surface, and, on account of the irregularity in the shape of the pieces of iron, it is unlikely that such an oxide film, if it existed, would form a complete, unbroken protective coating.

Nevertheless, the presence of some kind of protective coating on the iron, capable of being dissolved by cold dilute hydrochloric acid and not by sulphuric acid or nitric acid under the same conditions, would explain why copper is deposited from a solution of copper chloride and not from copper sulphate or copper nitrate solutions; it would explain, too, why iron when subjected to pressure under copper sulphate and copper nitrate solutions causes the deposition of copper on it, for pressure might bring about a disruption of such a film; and further, it might be considered as an explanation of the fact that rise of temperature will cause copper to be deposited on the iron from copper sulphate and nitrate solutions, on the ground that such a film would be more soluble in hot than in cold acids.

There are two possible kinds of protective films which might conceivably be present on the surface of the pure iron, namely, (*a*) an oxide film produced by the reversible decomposition of small traces of water in the hydrogen used for the reduction of the iron oxide to iron, and (*b*) a protective layer of some hydride of iron produced by the absorption of the hydrogen as the metal cooled down in the gas.

Careful experiments have been made to test these possibilities. The hydrogen used for the reduction of the iron oxide was dried by passing it through a long tube containing phosphoric oxide, so as to remove all but the most minute traces of water, and then the iron which was produced was brought in contact with copper sulphate solution whilst it was still in the atmosphere of hydrogen. The copper sulphate solution itself had been previously saturated with pure hydrogen. There was no deposition of copper on the iron, which remained quite untarnished in the solution.

Other specimens of iron were prepared and allowed to come in contact with the air before they were cold. A thin, yellow layer of oxide was formed on the metal, but this slightly oxidised metal caused the immediate deposition of copper when placed in contact with a solution of copper sulphate.

It is probable that, as suggested above, the oxide film does not form a complete protective coating; in such a case there would be differences of potential on the surface of the iron, and we should expect copper to be deposited.

It must be concluded, then, that the non-deposition of copper by the pure iron from copper sulphate and copper nitrate solutions cannot be accounted for by the presence of a protective oxide film on the metal.

That the same argument holds good in the case of a possible protective film of hydride is proved by the fact that specimens of the metal which had been heated in a clear silica tube for several hours, at about 1000° in a vacuum, until spectroscopic tests showed that all the hydrogen had been removed, behaved in all respects as before—they remained quite bright and unaffected in contact with saturated solutions of copper nitrate and copper sulphate, but caused the immediate deposition of copper when placed in very dilute solutions of copper chloride.

The behaviour of the iron under different conditions towards solutions of the sulphate and nitrate of copper can be readily explained on the basis of an electrolytic theory, but the extraordinary behaviour of the metal in copper chloride solutions is mysterious.

We have seen that the chlorides of the alkali metals have a very remarkable action in starting and promoting the rusting of the pure iron in air, and it may be that soluble chlorides have the power, in some way or other, of increasing the electrical differences which exist in the iron. If the chloridion has such a property it would also explain this curious behaviour of copper chloride. For the present this must be left an open question.

Behaviour of Pure Iron towards the Ferroxyl Reagent.—This shows in a most striking manner the difference between this iron and all commercial forms of the metal or of iron made by other laboratory methods.

It has been stated above that if a piece of commercial iron is placed in contact with an electrolyte (such as a solution of sodium chloride) and a little phenolphthalein added, a pink colour is developed in the electrolyte at some portions only of the metallic surface, and that on keeping in air corrosion takes place at the other portions of the metal. This observation was first made by Cushman in 1907. Walker (*J. Amer. Chem. Soc.*, 1907, **29**, 1257) suggested that the addition of a little potassium ferricyanide to the reacting solution would act as an indicator for the ferrous ions, owing to the formation of Turnbull's blue, and would show that iron was passing into solution at the parts not coloured by the pink of the phenolphthalein.

It was further suggested that the use of gelatin or agar-agar so as to form a stiff jelly would prevent diffusion to some extent, and so preserve the colour effects.

This jelly containing a small quantity of phenolphthalein and potassium ferricyanide is called the ferroxyl reagent (Cushman and Gardner, "Corrosion and Preservation of Iron and Steel," p. 48 *et seq.*). It affords a very delicate and beautiful method of showing that all ordinary forms of iron are not physically homogeneous—that there are, on the surface of every piece of such metal, some points which are relatively electropositive to the rest—that the solution-pressure of the iron is greater at some points of the metallic surface than at others.

Cushman states that no iron has been found of such purity that it gives no trace of what he calls "positive and negative nodes" when treated with the ferroxyl reagent.

The author's pure iron remains quite bright, and causes no formation of "positive and negative nodes" when left in contact with the reagent for an indefinite time.

If a piece of the pure metal is subjected to pressure, however, it behaves like other kinds of iron when put in contact with the ferroxyl reagent. A pink colour develops in the jelly around the pressed part, and Turnbull's blue is formed round the parts which have not been subjected to pressure.

This shows again that in the pure iron the small differences of potential on the surface cannot give rise to a sufficiently large electromotive force to cause perceptible electrolysis, even in the presence of oxygen, but that the production by means of pressure of strained and unstrained parts in the iron gives rise to differences of potential of sufficient magnitude to cause perceptible electrolysis.

It has been stated earlier that passive iron can be left in contact with pure water and air free from acid constituents, without undergoing corrosion, and that it can be treated with copper sulphate (in very dilute solution) without causing the deposition of copper, for some time. It may be that passive iron has what we may describe as an "electrically equable surface"—that substances which produce this passivity in ordinary commercial iron reduce in some way or other the differences of electric potential which exist in all forms of iron hitherto investigated, and so diminish the tendency for perceptible electrolysis to take place when such iron is exposed to the action of air and an electrolyte.

That passivity can be produced in iron by many widely-different compounds indicates that there is probably more than one kind of passivity. It seems possible that the production of a completely protective coating of any kind, provided it is itself homogeneous in character, would be sufficient to explain most of the properties of passive iron.

It is a striking fact that, in the preparation of pure iron by the author's method, the same sample of ferric nitrate, treated in exactly the same manner throughout its conversion into iron, will not always give like specimens of the metal.

Some of the iron produced will remain in contact with water exposed to air for an apparently indefinite time without showing any signs of corrosion, whilst other specimens will show corrosion in a few hours. The difference in behaviour cannot be due to differences in chemical composition. The only variable factors in the preparation are temperature and rate of cooling, and so any differences would probably be physical differences. All the specimens of iron show exactly the same external structure when examined under the microscope.

One might expect to find some sort of gradation in the liability to corrosion of different samples of the iron, but a long experience has proved that the iron will either show signs of corrosion in a few hours or will remain quite bright for an indefinite period when exposed to the action of air and water.

Gradations in behaviour are, however, brought out by the action of salts. Some specimens of iron were taken which had remained uncorroded in contact with air and water for several months; they were then placed in dilute solutions of sodium chloride of different concentrations in quartz tubes and exposed to the air.

The experiments, which are only preliminary in character, showed curious differences in the behaviour of the iron. Some specimens remained uncorroded in $N/20$-solutions for several days, whilst others corroded quickly in $N/50$- and $N/100$-solutions. All the specimens of iron, as mentioned above, had previously remained free from corrosion when exposed to the action of air and water for a long period.

Similar gradations are found in the behaviour of the iron towards solutions of copper sulphate and copper nitrate.

Pieces of iron which will not rust when exposed to water and air will not cause the deposition of copper when placed in contact with solutions of the sulphate or the nitrate of copper. The converse is also true.

One most interesting case has, however, been encountered. A piece of iron which had not rusted on long exposure to the action of air and water was placed in a strong solution of copper nitrate, and after some time it was found that beautiful crystals of copper had been deposited on parts of the iron, whilst other parts had remained quite unaffected.

It seems probable, then, that the fundamental cause of the corrosion of iron is not carbonic acid or any other acid, and that the cause is rather to be sought in differences of solution-pressure of different parts of the iron—differences which persist even in the most highly purified specimens of the metal.

My thanks are gratefully tendered to the Goldsmiths' Company and to the Government Grant Committee of the Royal Society for grants in aid of these investigations, and also to Professor J. S. Townsend, who generously supplied me with liquid air.

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CCXVII.—*The Oxidation of Some Benzyl Compounds of Sulphur. Part I.*

By JOHN ARMSTRONG SMYTHE.

IN a recent paper describing the preparation and reactions of benzyl tri- and tetra-sulphides (Smythe and Forster, Trans., 1910, **97**, 1195), it was stated that both of the compounds are oxidised by hydrogen peroxide. The study of these reactions has led to some unexpected results, the investigation of which is still in progress. Meanwhile, a number of the benzyl compounds of sulphur have been submitted to the action of hydrogen peroxide in the hope that, thereby, some light would be thrown on the main problem, and the results of this work are embodied in the present communication.

The compounds studied so far are the sulphide, sulphoxide, sulphone, disulphide, disulphoxide, and mercaptan of benzyl, and the mixed sulphide, benzoyl benzyl sulphide. Of these, only the sulphone is stable in contact with hydrogen peroxide. The sulphide is quantitatively oxidised to the sulphoxide or the sulphone, according to the amount of oxidising agent present, and the sulphoxide is converted into the sulphone.

In marked contrast to these monosulphidic compounds are those which contain two, three, or four atoms of sulphur linked together. Oxidation of such compounds always results in rupture, to a certain extent, of the sulphur atoms, and in the formation of benzaldehyde and the monosulphidic compounds, sulphuric and benzylsulphonic acids. There is, however, a limit to the degree of rupturing possible, for it is found that the amount of sulphuric acid formed in the reaction is approximately constant, although the other products may vary in quantity to a considerable extent.

To take an example, benzyl disulphide gives on oxidation benzyl disulphoxide, benzaldehyde, sulphuric and benzylsulphonic acids. The yields of disulphoxide in four experiments were 12, 56, 64, and 72 per cent. of the weight of material oxidised, and the yields of sulphuric acid, calculated on the disulphide, completely oxidised, that is, beyond the disulphoxide stage, were 17·7, 13·5, 13·1, 16·8 per cent. respectively.

In seeking for an explanation of this behaviour of the disulphide, two facts appear of importance; first, that the attainment of the full valency of the sulphur in the benzyl compounds is only possible in the case of the monosulphide; secondly, that the disulphoxide has been shown by Fromm and Palma (*Ber.*, 1906, **39**, 3308) to be capable of hydrolytic decomposition. We may conceive, then, the first stages of the reaction between benzyl disulphide and hydrogen peroxide to consist in the oxidation to disulphoxide and the hydrolysis of this compound according to the equation:

$$CH_2Ph\cdot SO\cdot SO\cdot CH_2Ph + H_2O = CH_2Ph\cdot S\cdot OH + CH_2Ph\cdot SO_2H.$$

One of the products of hydrolysis, namely, the compound $CH_2Ph\cdot S\cdot OH$, has never been isolated, although its transient existence has been postulated by a number of chemists (for example, Fromm and Smiles). It would probably be immediately oxidised by hydrogen peroxide to benzylsulphonic acid, $CH_2Ph\cdot SO_3H$. The other product, benzylsulphinic acid, has been studied by Fromm and Palma, who were unable to analyse it owing to its instability. The substance was found to decompose spontaneously, especially in acid solutions, into benzyl disulphoxide, benzaldehyde, and sulphur dioxide. The probable equation expressing this decomposition is, according to Fromm and Palma (*loc. cit.*):

$$5CH_2Ph\cdot SO_2H = 2(CH_2Ph)_2S_2O_2 + Ph\cdot CHO + SO_2 + 3H_2O.$$

In the presence of hydrogen peroxide, sulphur dioxide would be immediately oxidised to sulphuric acid. This series of reactions would, therefore, account in a simple manner for all the products of oxidation of benzyl disulphide, and, as will be seen later, of the disulphoxide, mercaptan, and benzoyl benzyl sulphide as well.

This hypothesis may also be developed from the quantitative side. Summing up all the individual equations, the reaction between the disulphoxide and hydrogen peroxide may be represented thus:

$$5(CH_2Ph)_2S_2O_2 + 11H_2O_2 = \\ 5CH_2Ph\cdot SO_3H + 2(CH_2Ph)_2S_2O_2 + Ph\cdot CHO + H_2SO_4 + 8H_2O.$$

Of the five molecules of disulphoxide, two are thus regenerated, and the summation of an infinite number of cycles of such reactions yields the result that $8\frac{1}{3}$ gram-molecules of sulphonic acid and $1\frac{2}{3}$ gram-molecules of sulphuric acid are producible from 5 gram-molecules of the disulphoxide (or its equivalent of disulphide, mercaptan, etc.). The yield of sulphuric acid in the oxidation of these compounds can thus be calculated; it amounts to 13·2 per cent. in the case of the disulphide, 13·1 per cent. for the mercaptan, and 7·2 per cent. for the benzoyl benzyl sulphide.

The mean value found for the disulphide was 15·2; four determinations made in the case of the mercaptan gave the values 12·4, 14·3, 13·4, and 12·6, the mean of which is 13·2; and two determinations in the case of the benzoyl compound gave 6·8 and 8·4 per cent. (mean 7·6). When the experimental difficulties are borne in mind, the agreement is fairly satisfactory, and gives some support to the hypothesis.

The reaction between benzyl mercaptan and hydrogen peroxide affords an excellent example of step-wise oxidation, benzyl disulphide, benzyl disulphoxide, and benzylsulphonic acid being successively formed. The two solids crystallise out in turn, evolution of heat accompanying the production of each compound. From the course of the reaction it is evident that the sulphonic acid is derived, in part at least, from the disulphoxide. The possibility of direct oxidation of the mercaptan to sulphonic acid would seem to be excluded in view of the large amount of sulphuric acid formed in the reaction; the yield of this being, as pointed out above, almost the same as that obtained from an equivalent weight of benzyl disulphide.

The substitution of a benzyl by a benzoyl group in the monosulphide does not favour the production of benzaldehyde by oxidation, for the chief product in the oxidation of benzoyl benzyl sulphide is benzoic acid. The amount of this and the rapidity with which it is formed leave no doubt that it is a primary product, and not the result of the oxidation of benzaldehyde initially formed. The other products of reaction are benzylsulphonic acid, sulphuric acid, benzaldehyde, and benzyl disulphoxide—all compounds resulting from the oxidation of benzyl mercaptan. There can be no doubt, then, that the benzoyl compound behaves as an ester, being first hydrolysed as shown by the equation:

$$COPh{\cdot}S{\cdot}CH_2Ph + H_2O = Ph{\cdot}CO_2H + CH_2Ph{\cdot}SH$$

and that the mercaptan thus set free is oxidised as already described.

Reviewing briefly the results of this investigation, one sees in these reactions, carried out with similarly constituted compounds and under similar conditions, a two-fold tendency at work, namely, the striving of the sulphur atom to become fully oxidised, and its inability to become so, in the polysulphidic combinations, with resulting rupture of the molecule and degradation into monosulphidic compounds. From a consideration of the facts which are being slowly accumulated on this subject, it would appear that the reason for this inability is, in part at least, steric, but this cannot be stated definitely in the present state of our knowledge.

EXPERIMENTAL.

The method used throughout the course of this work is, with few slight modifications, the following. From 5 to 10 grams of the compound to be studied are dissolved in 20 to 100 c.c. of glacial acetic acid, and a measured volume of hydrogen peroxide solution (30 per cent.) is added. The reaction sometimes starts quickly with considerable development of heat, sometimes so slowly as not to be perceptible, and in all cases without evolution of oxygen. The solid products crystallise out in part and are collected, and the liquors are deprived of excess of acetic acid by keeping in a vacuum desiccator over solid potassium hydroxide, small quantities of water being added from time to time to complete the precipitation of solid matter. The residual liquors from these operations are either warmed and treated with barium carbonate, the barium sulphate produced being determined and the barium benzylsulphonate obtained by crystallisation, or they are distilled in a current of steam and the benzaldehyde in the distillate is identified and determined by precipitation with phenylhydrazine. The determination of benzaldehyde by this method has but little quantitative significance, as control experiments show that the aldehyde is oxidised by hydrogen peroxide under the conditions in which it formed, the loss amounting on the average to 60 per cent. The sulphate determinations are more accurate, especially when the amount of hydrogen peroxide used is such that little or none remains after the completion of the reaction.

Benzyl Sulphide.—The reaction of this compound with hydrogen peroxide is rapid, and accompanied by considerable disengagement of heat; 5 grams of the sulphide and one equivalent of the peroxide yielded 5 grams of benzyl sulphoxide, melting after recrystallisation at 134°. Beyond a trace of sulphuric acid in the liquors, there are no secondary products of this reaction. (Found, S=13·69. $C_{14}H_{14}OS$ requires S=13·94 per cent.)

With excess of hydrogen peroxide (4 equivalents) oxidation of the sulphide is carried a stage further, benzyl sulphone being formed. Five grams of the sulphide yielded 5 grams of oxidation products, consisting largely of the sulphone with a small amount of sulphoxide. The sulphone, purified by crystallisation, melted at 151°. (Found, S=13·03. $C_{14}H_{14}O_2S$ requires S=13·04 per cent.)

The oxidation of benzyl sulphide with hydrogen peroxide is thus a very simple process, the sulphoxide or sulphone being formed quantitatively according to the amount of oxidising agent present. It is all the more remarkable, in view of this simplicity, that error should have crept into the literature of this subject. Hinsberg (*Ber.*, 1908, **41**, 2838) could find no trace of benzyl sulphone among the oxidation products of the sulphide, even when excess of hydrogen peroxide was employed, and on this alleged fact is founded an argument in favour of the symmetrical constitution of the disulphoxides. Prominence has further been given to the error, although unwittingly on the part of the authors, in a recent publication by Fichter and Wenk (*Ber.*, 1912, **45**, 1373).

Benzyl Sulphoxide.—As might be expected from the foregoing reaction, this compound is readily oxidised to benzyl sulphone. Five grams of sulphoxide and 10 c.c. of hydrogen peroxide in the presence of 25 c.c. of acetic acid yielded 5·2 grams of benzyl sulphone, melting at 151°. (Found, S=12·89. $C_{14}H_{14}O_2S$ requires S=13·04 per cent.) There was no appreciable liberation of heat, and no secondary products were detected.

Benzyl sulphone is quite unaffected by hydrogen peroxide, even after prolonged heating to 100°; it can be quantitatively recovered from the solution, which contains the merest trace of sulphuric acid.

Benzyl Disulphide.—The oxidation of this compound by hydrogen peroxide, in acetic acid solution, was studied by Hinsberg (*Ber.*, 1908, **41**. 2839), who presumably isolated the disulphoxide from the solid products of reaction. The liquors from these were stated, by this author, to contain small quantities of a compound with a lower melting point than the disulphoxide. This was possibly unaltered disulphide.

The reaction frequently sets in suddenly, especially if the materials are well shaken. Sometimes two distinct phases of oxidation can be detected, one corresponding with the crystallisation of disulphoxide, the other to the passing of this into solution, and each is accompanied by the liberation of heat. The products of reaction are benzyl disulphoxide (m. p. 108°; Found, S=23·10. $C_{14}H_{14}O_2S_2$ requires S=23·06 per cent.), benzylsulphonic acid (Found, Ba in barium salt=26·56; $(C_7H_7{\cdot}SO_3)_2Ba,2H_2O$ requires Ba=26·60 per cent.), sulphuric acid, and benzaldehyde.

Minute quantities of an evil-smelling substance, which clings obstinately to the disulphoxide during crystallisation, but is destroyed, apparently with the liberation of sulphur, by prolonged warming of the solution, are also produced in this reaction. The relative quantities in which the products are formed depends on the amount of oxidising agent present. With one equivalent of hydrogen peroxide, the yield of disulphoxide is 78 per cent., and but little sulphonic acid is produced; with three equivalents of hydrogen peroxide, only 12 per cent. of disulphoxide is formed, but the yield of sulphonic acid rises to 60 per cent. The yield of benzaldehyde varies from 6 to 9 per cent.; that of sulphuric acid is, on the average, 15 per cent. of the weight of disulphide taken.

Benzyl Disulphoxide.—This is oxidised very slowly in the cold, possibly by reason of its sparing solubility. If the reaction is started by gently warming, it proceeds with vigour. The products are benzylsulphonic acid, sulphuric acid, and benzaldehyde. On one occasion, minute quantities of a solid melting at 170° were obtained, but the amount was too small for analysis, and subsequent attempts to prepare it failed. The yield of benzaldehyde is about 3 per cent., and of sulphuric acid 11 per cent. In one experiment, 5 grams of the disulphoxide furnished 7·6 grams of pure barium benzylsulphonate (Found, Ba=26·6. $(C_7H_7\cdot SO_3)_2Ba,2H_2O$ requires Ba=26·6 per cent.), which corresponds with a yield of 92 per cent. of the free acid. The maximum yield in terms of the hypothesis sketched in the introduction is 102 per cent.

Benzoyl Benzyl Sulphide.—The behaviour of this mixed sulphide with hydrogen peroxide is very different from that of the dibenzyl sulphide, for, as already mentioned, the evidence all points to primary hydrolysis followed by oxidation of the mercaptan, which is one of the decomposition products. The method of working adopted is somewhat different from the ordinary one, and may be illustrated by briefly recounting the procedure in one experiment.

Five grams of the compound were dissolved in 25 c.c. of acetic acid, and 5 c.c. of hydrogen peroxide added. The solution became warm after an hour's interval, and remained warm for over an hour. Next day, the excess of acetic acid was removed by evaporation over potassium hydroxide, water added, and the liquid extracted with ether. The aqueous portion was treated with barium carbonate, filtered from the excess of this reagent and barium sulphate, and the soluble salt obtained by crystallisation from the filtrate. This proved to be barium benzylsulphonate. (Found, Ba=26·65. $(C_7H_7\cdot SO_3)_2,2H_2O$ requires Ba=26·60 per cent.)

The ethereal portion was washed with sodium carbonate solution and allowed to evaporate. It deposited about 1 gram of unaltered benzoyl compound (m. p. 38°), and a small amount of acicular crystals melting at 108°. A mixed melting-point determination proved this substance to be benzyl disulphoxide, whilst benzoic acid was obtained from the alkaline extract (m. p. 121°; Found, Ag in silver salt=47·30. Calc., Ag=47·15 per cent.).

The yields of the various products obtained in other trials were: benzoic acid, 43 per cent.; benzaldehyde, 1 and 2 per cent.; sulphuric acid, 6·8 and 8·4 per cent.

Benzyl Mercaptan.—There are three distinct stages in the oxidation of the mercaptan by hydrogen peroxide. The solution quickly becomes warm, then an emulsion is formed, and crystals separate after about fifteen minutes. In the next stage, these crystals dissolve, more heat is developed, and fresh crystals appear; this stage occupies about an hour. Finally, the crystals pass slowly into solution, and at the end of a few days the liquid is clear again. The solid produced in the first stage of reaction melts, after purification, at 71°, and is benzyl disulphide (Found, S=25·83;

$C_{14}H_{14}S_2$ requires S=26·07 per cent.); that formed in the second stage melts at 108°, and is benzyl disulphoxide. (Found, S=22·90; $C_{14}H_{14}O_2S_2$ requires S=23·03 per cent.)

The clear solution, worked up in the usual way, yields barium benzylsulphonate. (Found, Ba=26·60. $(C_7H_7\cdot SO_3)_2Ba,2H_2O$ requires Ba=26·60 per cent.)

The yield of the sulphonic acid amounts (with four equivalents of hydrogen peroxide) to 72 per cent.; of benzaldehyde, from 7 to 14 per cent.; of sulphuric acid, 13 per cent. With deficiency of hydrogen peroxide (two equivalents), the yield of sulphonic acid is small, whilst that of disulphoxide rises to 48 per cent.

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

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CCXVIII.—*Studies of Chinese Wood Oil. β-Elaeostearic Acid.*

By Robert Selby Morrell.

The so-called elæostearic acid has been investigated by Cloëz (*Compt. rend.*, 1876, **82**, 501), Maquenne (*ibid.*, 1902, **135**, 696), Kametaka (Trans., 1903, **83**, 1042), Fokin (*Zeitsch. Elektrochem.*, 1906, **12**, 759), and Majima (*Ber.*, 1909, **42**, 674; 1912, **45**, 2730). Cloëz assigned to the acid the formula $C_{17}H_{30}O_2$, and named it elæomargaric acid. Maquenne and Kametaka showed that the acid must contain eighteen carbon atoms, the former maintaining the formula $C_{18}H_{30}O_2$ from the results of careful analyses of the free acid, the latter preferring the formula $C_{18}H_{32}O_2$, since a tetrabromo-acid was obtained identical with that prepared from linolic acid. Majima obtained *n*-valeraldehyde, azelaic, and valeric acids as decomposition products of the ozonide of elæostearic acid, and found that elæostearic acid was transformed quantitatively into stearic acid by catalytic reduction. He consequently assigned the constitution $CH_3\cdot[CH_2]_3\cdot CH{:}CH\cdot[CH_2]_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$ to elæostearic acid, a conclusion also in harmony with the results described in this paper. The presence of a conjugated double linking is consistent with the tendency of wood oil to become polymerised when heated. Maquenne has shown that the action of a trace of sulphur on wood oil or the free acid causes probably a stereoisomeric change whereby an acid (m. p. 71°) is formed, differing from elæostearic acid (m. p. 48°) in resistance to oxidation. The same acid was produced when elæostearic acid was exposed to light. Cloëz (*Bull. Soc. chim.*, 1876, [ii], **26**, 286; 1877, [ii], **28**, 24) states that wood oil when exposed to light gives an isomeric glyceride (m. p. 32°).

The results of a further investigation of the glyceride produced when Chinese wood oil is exposed to light confirm many of the statements of previous investigators.

β-Elæostearic acid (m. p. 72°) and its glyceride (m. p. 48°) are stereoisomerides of elæostearic acid (m. p. 48°) and its liquid glyceride. With the exception of the potassium salt, the derivatives of the acid absorb oxygen with rapidity, and in several cases it was impossible to prevent oxidation before analysis.

The yield of the tetrabromo-acid (m. p. 115°) is very small, and the main product of the bromination is an oily tetrabromide.

The investigation of the properties of β-elæostearic acid (m. p. 72°) has shown that it is possible to obtain definite salts characterised by great insolubility in water. The ethyl ester can be distilled under diminished pressure, and undoubtedly contains only two double linkings. The low values of the hydrogen in Maquenne's analyses must be ascribed to unavoidable oxidation during the manipulation of the acid and of its derivatives.

The study of a crystalline glyceride of a drying oil may help to throw light on the changes which occur when a drying oil is exposed to air. Some interesting results have been obtained which tend to confirm the view that polymerisation occurs during the drying of an oil.

Further investigation is in progress, and the results will be communicated in a subsequent paper.

EXPERIMENTAL.

Hankow Chinese wood oil was exposed to light in glass bottles fitted with air-tight stoppers. In a few days, depending on the season, crystals appeared, and in a year about 6 per cent. of the oil was transformed into a crystalline modification. In the dark the oil was unchanged. After treatment with acetone the crystals were collected, and washed with the solvent to remove the last traces of oil.

The solid was dried in a vacuum, and melted at 61—62°. The oil in the filtrate after removal of the acetone by distillation in a current of carbon dioxide was again exposed to light, and in a few days yielded another crop of crystals.

By repetition of the process a very considerable proportion of the wood oil was transformed; in fact, when the crystallisation had been started, treatment with acetone accelerated the change when the oil was exposed again to light.

The white solid is soluble in chloroform, ether, or benzene, but very sparingly so in cold alcohol (10 grams dissolve in 200 c.c. of boiling alcohol). It is readily soluble in hot glacial acetic acid, and separates out on cooling the solution. By solution in benzene and precipitation by alcohol, crystalline rosettes of rounded plates were obtained, melting at 61—62°. Recrystallisation from hot alcohol or hot glacial acetic acid gave crystals melting at the same temperature. Although every precaution was taken to prevent absorption of oxygen, the results of a number of analyses show that it is impossible to decide between the formulæ $(C_{18}H_{29}O_2)_3C_3H_5$ and $(C_{18}H_{31}O_2)_3C_3H_5$. It was found that the substance slowly gained weight, even in a vacuum desiccator, which added to the difficulty in removing the last traces of the solvent:

0·1914 gave 0·5486 CO_2 and 0·1814 H_2O. C=78·2; H=10·55.
0·1052 „ 0·3028 CO_2 „ 0·100 H_2O. C=78·49; H=10·57.
Iodine value (Wijs)=183. Saponification value=191·5.
0·7952 in 14·9256 benzene gave $\Delta t = -0{\cdot}297°$. M.W.=879.
$(C_{18}H_{31}O_2)_3C_3H_5$ requires C=77·92; H=11·16 per cent.
Iodine value=173·5. M.W.=878.
$(C_{18}H_{29}O_2)_3C_3H_5$ requires C=78·45; H=10·55 per cent. I.V.=262.

The oxidised glyceride is quite insoluble in warm glacial acetic acid, so that the purity of the crystalline modification can be confirmed by its complete solubility in that medium. The avidity with which the substance takes up oxygen makes it necessary to keep it in sealed vessels. In an ordinary glass-stoppered bottle the percentages of carbon and hydrogen had fallen in four days from 78·2 and 10·55 to 72·5 and 9·53 respectively. Ten days afterwards the substance contained 64·63 per cent. of carbon and 8·59 of hydrogen. It could now be heated to 230° without melting, and with only a slight change in colour.

On exposure to air a decided odour of valeraldehyde was noticed, and when the weight had become constant the percentages of carbon and hydrogen had fallen to 63·9 and 8·70 respectively ($[C_{18}H_{31}O_6]_3C_3H_5$ requires C=64·0; H=9·15). When treated with potassium iodide and dilute acetic acid, iodine was liberated; on boiling with water the oxidised glyceride became yellow and spongy in texture, and the aqueous extract gave a decided coloration with Schiff's reagent and a yellow colour with titanium dioxide in dilute sulphuric acid.

It is evident that the products of oxidation include an aldehyde derived from the decomposition of a peroxide.

The original crystalline substance does not give these reactions. On exposure to air at the ordinary temperature the glyceride gained 12·15 per cent. in weight with loss of crystalline form, but without appreciable change in colour. The saponification value had risen to 412·9, and the iodine and acid values were 41·45 and 47·7 respectively.

When dry oxygen was passed over the crystalline glyceride, there was a steady increase in weight to 23 per cent., accompanied by the liberation of substances of an aldehydic and acidic nature, which were absorbed by alkali and ammoniacal silver nitrate.

When the temperature was raised to 100° and a current of dry oxygen or nitrogen was passed over the substance, there was an immediate change in colour, accompanied by a loss in weight to a constant value of 8 per cent., whilst the total gain in weight of the absorption tubes was 35 per cent. of the original weight of the substance. The final product reduced Fehling's solution, was readily soluble in alkalis, but it gave no reaction for a peroxide, and its iodine value had fallen to 38·35. Olsen and Ratner (*Eighth Int. Cong. Appl. Chem.*, 1912, Sect. Ve, Orig. Comm. 12, 165—173) have investigated the decomposition of linseed oil during drying under similar conditions.

Potassium β-Elaeostearate.—Saponification of the glyceride by alcoholic potassium hydroxide gives a crystalline potassium salt, insoluble in cold alcohol, but crystallising from hot alcoholic solution in long, rhombic plates (one part of the salt dissolves in 20 parts of boiling alcohol):

0·5666 gave 0·1566 K_2SO_4. K = 12·39.
0·4946 „ 0·1352 K_2SO_4. K = 12·26.
$C_{18}H_{31}O_2K$ requires K = 12·36 per cent.

The salt is partly hydrolysed when warmed in aqueous solution. An analysis of the salt recrystallised from hot water gave:

0·4122 gave 0·0530 K_2SO_4. K = 5·76.
$C_{18}H_{32}O_2,C_{18}H_{31}O_2K$ requires K = 6·24 per cent.

A solubility determination in water at 16·7° showed that 0·279 parts were present in 100 parts of solution.

The salt can be heated above 230° without change in colour. After recrystallisation from hot water the salt softens at 121° and melts to a jelly at 185°.

Its solubility in water is so small that it is impossible to transform it completely into the corresponding acid by the action of dilute acid in the presence of ether. The salt can be heated at 110° for an hour without change in weight, and on exposure to air at the ordinary temperature for fourteen days it gains only 5 per cent., and in twenty-one days the total gain is 5·5 per cent.; the salt becomes yellow, and acquires a greasy surface. With Schiff's reagent the crystals become purple, pure potassium iodide and dilute acetic acid liberate iodine, but on warming with dilute sulphuric acid, filtering, and testing with titanic acid no yellow coloration ensues.

It is evident that a peroxide is formed on exposure to air, which can be decomposed to give an aldehyde but no hydrogen peroxide.

β-Elaeostearic Acid.—Twenty grams of the potassium salt were dissolved in 600 c.c. of boiling water, and excess of dilute sulphuric acid was added; the acid separated out either as an oil or as a white, crystalline solid. In order to free it from any potassium salt it was dissolved in ether, and the ether distilled off in a current of carbon dioxide. The acid was recrystallised from warm alcohol or acetone, and separated from the former in tufts of needles, but from the latter solvent in laminæ with serrated edges. The melting point was 72°, which was constant after the first recrystallisation. There was no evidence of the presence of the modification of lower melting point:

0·1810 gave 0·5146 CO_2 and 0·1729 H_2O. C=77·5; H=10·6.
0·1072 „ 9·3046 CO_2 „ 0·1056 H_2O. C=77·47; H=10·94.
Iodine value (Wijs)=175·4; 180·7; 183·5.
M.W. (Landsberger)=283 and 306.
$C_{18}H_{32}O_2$ requires C=77·4; H=11·46 per cent. Iodine value=181·4. M.W.=280.
$C_{18}H_{30}O_2$ requires C=77·13; H=10·7 per cent.

It is not possible to decide between the two formulæ from an elementary analysis, because the same difficulties were experienced as in the case of the glyceride. Although the acid is easily soluble in warm glacial acetic acid, its solubility in the cold solvent is too small to allow of a determination of the lowering of the freezing point.

Ammonium β-Elaeostearate.—Five grams of the acid, recrystallised from alcohol, were dissolved in 100 c.c. of hot alcohol, and treated with excess of alcoholic ammonia. The ammonium salt separated from the solution in lustrous lamellæ; the yield of the pure salt was 4 grams:

2·1548 gave 0·0125 NH_3. NH_4=5·79.
$C_{18}H_{31}O_2NH_4$ requires NH_4=5·71 per cent.

The ammonium salt dissolves readily in warm alcohol or hot water, but hydrolysis occurs as in the case of potassium salt. It is insoluble in ether or cold water (100 parts of the aqueous solution contain 0·0443 parts of the salt).

Silver β-Elaeostearate.—A solution of silver nitrate was added to an alcoholic solution of the ammonium salt, and the white precipitate was washed with alcohol and ether and dried in a vacuum:

0·4999 gave 0·1389 Ag. Ag=27·82.

$C_{18}H_{31}O_2Ag$ requires Ag=27·9 per cent.

Calcium β-Elaeostearate.—A solution of calcium chloride was added to an alcoholic solution of the ammonium salt, and the white precipitate was washed with water until free from chlorides, and dried in a vacuum:

0·5162 gave 0·1208 $CaSO_4$. Ca=6·88.

$(C_{18}H_{31}O_2)_2Ca$ requires Ca=6·67 per cent.

Barium β-Elaeostearate.—The salt was prepared in the same way as the calcium salt; it was precipitated as a white, crystalline, granular substance, and dried in a vacuum:

0·5146 gave 0·174 $BaSO_4$. Ba=10·89.

$(C_{18}H_{31}O_2)_2Ba$ requires Ba=19·82 per cent.

Ethyl β-Elaeostearate.—The ethyl ester was obtained from the acid by the action of sulphuric acid and alcohol. Care must be taken to avoid excess of sulphuric acid, otherwise considerable darkening occurs during the reaction. The ethyl ester was obtained as a pale yellow oil, which absorbed oxygen so rapidly that it was difficult to remove the last traces of ether without the occurrence of oxidation. The preparation of the ester was performed in an atmosphere of carbon dioxide, and every precaution was taken to exclude oxygen:

0·1813 gave 0·5142 CO_2 and 0·1799 H_2O. C=77·35; H=11·02.
Iodine value=150·4.

$C_{20}H_{36}O_2$ requires C=77·9; H=11·66 per cent.
Iodine value=165.

The ethyl ester boiled at 232°/14 mm. without decomposition, although a considerable amount of a non-volatile oil (iodine value=94) was left, if air were allowed to pass into the flask during the distillation. An analysis of the distillate gave the following results:

0·1888 gave 0·5443 CO_2 and 0·1884 H_2O. C=77·18; H=11·98.
Iodine value=153—154.

0·8910 (in 12·7862 acetic acid) gave $\Delta t = -0·765$. M.W.=355·6.

$C_{20}H_{36}O_2$ requires M.W.=308.

Although carbon dioxide was passed into the flask during the distillation a slight oxidation of the ethyl ester occurred. Thionyl chloride could not be used for the preparation of the ester because a black, viscid mass was produced during the removal of the chloride.

On exposure to air at the ordinary temperature, ethyl β-elæostearate gained 10·24 per cent. in weight in twenty-four hours. The maximum increase was 12 per cent., which was followed by a loss in weight until a constant gain of 11·1 per cent. was obtained:

$C_{20}H_{36}O_2 + 2O$ requires gain = 10·39 per cent.

The oxidised oil reduced Fehling's solution slightly, and on treatment with Schiff's reagent became purple. When warmed with pure potassium iodide solution no iodine was liberated except on addition of a few drops of dilute sulphuric acid. The ester did not set, and remained clear; there was no matt surface, as in the case of Chinese wood oil.

Action of Bromine on β-Elaeostearic Acid.

β-Elæostearic acid (1 mol.), twice recrystallised from alcohol, was dissolved in five times its weight of glacial acetic acid, and after cooling to 0° bromine (4 atoms) was added slowly until a permanent coloration ensued. The solution, which fumed very slightly, was concentrated in a vacuum at 50°, until the acetic acid was removed. A pasty solid was left, which was freed from syrup by light petroleum. The yield was 20 per cent. of the acid taken. It was recrystallised several times from alcohol, and on cooling, bunches of fine needles were obtained, melting at 115°:

0·2073 gave 0·2728 CO_2 and H_2O. C = 35·89; H = 5·0.
0·2404 „ 0·3022 AgBr. Br = 53·4.
$C_{18}H_{32}O_2Br_4$ requires C = 36·0; H = 5·33; Br = 53·3 per cent.

The tetrabromo-acid is very soluble in benzene or carbon tetrachloride, and can be recrystallised from ethyl acetate or methyl alcohol. Bromination of β-elæostearic acid in light petroleum solution gave a 33 per cent. yield of crude tetrabromo-acid, but the product was contaminated with a syrupy substance, which reduced the yield of the pure crystallised acid.

An analysis of the uncrystallisable syrup gave the following numbers:

0·2528 gave 0·3156 AgBr. Br = 52·8.
$C_{18}H_{32}O_2Br_4$ requires Br = 53·3 per cent.

Both the crystalline and syrupy tetrabromo-acids are saturated, because treatment with iodine trichloride in the form of Wijs' solution showed no further addition of halogen.

Oxidation of β-Elaeostearic Acid by Potassium Permanganate.

The oxidation of the potassium salt was performed according to the directions given by Hazura and Kametaka. Owing to the sparing solubility of the salt a very dilute solution was used, and the total bulk of the solution was about 6 litres for 25 grams of the potassium salt. The precipitate obtained on acidifying with sulphurous acid was viscid and soluble in ether. It reduced Fehling's solution, gave a purple colour with Schiff's reagent, and liberated iodine from pure potassium iodide.

The yield of crystalline, insoluble hydroxy-acids from the oxidation of the acids of linseed oil under similar conditions was found to be 20 per cent. of the acids taken.

Concentration of the filtrate from the first precipitate gave azelaic acid contaminated with its aldehyde. It was necessary to repeat the oxidation with potassium permanganate to obtain the pure acid melting at 105—106° (Found, $C=57\cdot88$; $H=8\cdot43$. $C_9H_{16}O_4$ requires $C=57\cdot44$; $H=8\cdot43$ per cent.).

The yield of azelaic acid was nearly 5 grams.

The acid filtrate contained a volatile acid, which was separated by distillation in a current of steam. It possessed the characteristic odour of *n*-valeric acid (Found, Ag in silver salt $=51\cdot44$. $C_5H_9O_2Ag$ requires $51\cdot67$ per cent.).

After the removal of azelaic and valeric acids the solution was examined for tartaric and succinic acids. Hydrogen peroxide and ferrous sulphate gave no coloration, which showed the absence of tartaric acid. The pyrrole reaction for succinic acid was obtained especially in the presence of zinc dust. Neuberg (*Chem. Zentr.*, 1904, ii, 1436) states that azelaic acid gives the pyrrole reaction with zinc dust, so that the test cannot be considered as quite decisive for the presence of succinic acid derivatives.

The solution was neutralised with ammonia, and silver nitrate added; the colourless silver salt was washed with water, alcohol, and ether, and dried in a vacuum:

0·3977 gave 0·1863 Ag. $Ag=46\cdot8$ per cent.

The low percentage of silver confirmed the absence of tartaric and succinic acids. The silver salt was probably a mixture of azelaic and valeric acids which would contain 50·4 and 51·4 Ag respectively.

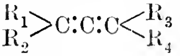
I desire to express my thanks to Messrs. Mander Brothers for permission to publish the results of this investigation.

Mander Brothers,
Wolverhampton.

CCXIX.—*The Condensation of Pentaerythritol with Aldehydes.*

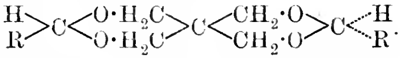
By JOHN READ.

VAN'T HOFF'S conception that substances of the type



$$\begin{matrix}R_1\\R_2\end{matrix}\!>\!C{:}C{:}C\!<\!\begin{matrix}R_3\\R_4\end{matrix}$$

should possess enantiomorphism of molecular configuration, and hence should be capable of exhibiting optical activity in the amorphous condition, has not yet been realised experimentally, owing chiefly to the chemical instability of such compounds. The more stable substances derived structurally from the above by substituting a ring-system for one of the ethylene linkings have, however, been utilised successfully in the experimental proof of van't Hoff's assumption (Perkin, Pope, and Wallach, Trans., 1909, **95**, 1789; Mills and Bain, Trans., 1910, **97**, 1866). Structurally, substances of the latter type occupy an intermediate position between the allene derivatives imagined by van't Hoff and the condensation products of pentaerythritol described below. In the last class of compounds each of the original ethylene linkings has been replaced by a ring-system; a third class of compounds is thus arrived at which should possess enantiomorphism of molecular configuration, despite the fact that no particular atom in the molecule can be identified as asymmetric. From an inspection of the general structural formula of these substances it is also apparent that such enantiomorphism will be due to the asymmetric distribution in space of only two kinds of groups:



$$\begin{matrix}H\\R\end{matrix}\!>\!C\!<\!\begin{matrix}O\cdot H_2C\\O\cdot H_2C\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}\!>\!C\!<\!\begin{matrix}H\\R\end{matrix}.$$

Similar considerations hold for the *spiro*cyclane derivatives described by Fecht (*Ber.*, 1907, **40**, 3888).

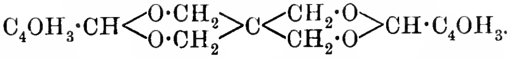
As no case of optical activity has been hitherto realised which is traceable to the possession of an enantiomorphous molecular configuration of the type just indicated, several such substances were prepared in the hope that one or more might be found which could be resolved into optically active components by mere crystallisation. In every case, however, the compounds were so sparingly soluble in the ordinary solvents and formed such small crystals that the Pasteur method of spontaneous resolution by crystallisation could not be applied; the substances are therefore now briefly described for the purpose of directing attention to the important type of enantiomorphism of molecular configuration which they represent.

Apparently the only compounds of this class which have been prepared are dimethylenepentaerythritol (Schulz and Tollens, *Annalen*, 1896, **289**, 28) and dibenzylidenepentaerythritol (Apel and Tollens, *ibid.*, 35). The condensation between pentaerythritol and aldehydes in general takes place readily in the presence of sulphuric acid of from 30 to 50 per cent. concentration. The products are very stable, and are, as a rule, remarkable for their sparing solubility, chloroform being the only solvent which is generally applicable. It is noteworthy that certain aldehydes cannot be caused to react with pentaerythritol; in this connexion it seems that a hydroxyl group in a neighbouring position to the aldehydic group exerts an inhibiting influence.

In continuation, it is proposed, by employing suitable substituted aldehydes, to prepare similar compounds containing an acidic or basic group, which should thus be capable of resolution into optically active components by crystallisation with optically active bases or acids in the usual manner.

EXPERIMENTAL.

Difurfurylidenepentaerythritol,



$$C_4OH_3\cdot CH{<}\begin{matrix}O\cdot CH_2\\O\cdot CH_2\end{matrix}{>}C{<}\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}{>}CH\cdot C_4OH_3.$$

Condensation occurs readily when furfuraldehyde is shaken with the requisite quantity of pentaerythritol dissolved in 30 per cent. sulphuric acid. The product is collected, washed with water, and crystallised from hot alcohol. It forms small, colourless plates, melting at 161°, which are readily soluble in most organic solvents, with the exception of ether and light petroleum:

0·1785 gave 0·4010 CO_2 and 0·0880 H_2O. C=61·27; H=5·52.
$C_{15}H_{16}O_6$ requires C=61·62; H=5·52 per cent.

Diheptylidenepentaerythritol, $C_5H_8O_4(CH\cdot[CH_2]_5\cdot CH_3)_2$, is easily formed in the presence of 30 per cent. sulphuric acid. After collection and subsequent washing with cold water, the substance is dissolved in warm aqueous alcohol, from which on keeping it is deposited in large, lustrous laminæ, melting at 63°. It is more readily soluble than the foregoing product:

0·2032 gave 0·5190 CO_2 and 0·2025 H_2O. C=69·66; H=11·15.
$C_{19}H_{36}O_4$ requires C=69·45; H=11·05 per cent.

Dibenzylidenepentaerythritol, $C_5H_8O_4(CH\cdot C_6H_5)_2$, crystallises from alcohol or chloroform in small plates melting at 160° (Apel and Tollens, *loc. cit.*). It is readily soluble in acetone, ethyl acetate, benzene, or chloroform, moderately so in hot alcohol, and practically insoluble in ether or light petroleum; large crystals of the substance could not be prepared.

*Di-*o-*nitrodibenzylidenepentaerythritol*, $C_5H_8O_4(CH{\cdot}C_6H_4{\cdot}NO_2)_2$, and the two isomeric substances described below are best prepared by shaking a warm mixture of the calculated amounts of the aldehyde and pentaerythritol dissolved in 50 per cent. sulphuric acid. The crystalline product is collected, washed with hot water, and crystallised from boiling alcohol, in which the ortho-derivative is only sparingly soluble. It forms long, silky, pale yellow needles, melting at 163—164°, which change to a pale green on exposure to light. The substance is much more readily soluble than the isomeric derivatives; it dissolves freely in acetone, ethyl acetate, benzene, or chloroform, but is insoluble in ether or light petroleum:

0·1523 gave 0·3140 CO_2 and 0·0610 H_2O. C=56·23; H=4·48.

$C_{19}H_{18}O_8N_2$ requires C=56·69; H=4·51 per cent.

*Di-*p-*nitrodibenzylidenepentaerythritol* crystallises from hot alcohol or ethyl acetate in small, pale yellow scales, melting at 229°. It is sparingly soluble in benzene or hot alcohol, and is the sole derivative described in the present paper which is only sparingly soluble in chloroform. It is moderately soluble in acetone or ethyl acetate:

0·1371 gave 0·2820 CO_2 and 0·0565 H_2O. C=56·10; H=4·61.

$C_{19}H_{18}O_8N_2$ requires C=56·69; H=4·51 per cent.

*Di-*m-*nitrobenzylidenepentaerythritol* separates from hot alcohol in minute needles melting at 185°. Unlike the ortho- and para-derivatives, it is colourless. It dissolves sparingly in hot alcohol, and is moderately soluble in acetone, ethyl acetate, benzene, or chloroform:

0·1485 gave 0·3060 CO_2 and 0·0600 H_2O. C=56·20; H=4·52.

$C_{19}H_{18}O_8N_2$ requires C=56·69; H=4·51 per cent.

Dicinnamylidenepentaerythritol, $C_5H_8O_4(CH{\cdot}CH{:}CH{\cdot}C_6H_5)_2$, is prepared in the customary manner by using 30 per cent. sulphuric acid as the condensing agent. It is moderately soluble in the usual organic solvents, and crystallises from hot alcohol in small scales melting at 195°:

0·1775 gave 0·4910 CO_2 and 0·1055 H_2O. C=75·44; H=6·65.

$C_{23}H_{24}O_4$ requires C=75·79; H=6·64 per cent.

Dianisylidenepentaerythritol, $C_5H_8O_4(CH{\cdot}C_6H_4{\cdot}OMe)_2$, prepared in presence of 30 per cent. acid, crystallises in fine scales from hot alcohol, in which it is moderately soluble. It dissolves readily in acetone, ethyl acetate, benzene, or chloroform, and melts at 177°:

0·1795 gave 0·4423 CO_2 and 0·1043 H_2O. C=67·20; H=6·50.

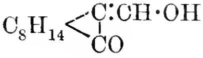
$C_{21}H_{24}O_6$ requires C=67·71; H=6·50 per cent.

Dipiperonylidenepentaerythritol, $C_5H_8O_4(CH{\cdot}C_7H_5O_2)_2$.—For the purpose of preparing this substance in a state of purity it is advisable to use excess of piperonal in the presence of 50 per cent. sulphuric acid. By warming the mixture on the water-bath and shaking continuously, a hard mass is eventually obtained on cooling. This is broken up and crystallised from hot alcohol, and is subsequently freed from pentaerythritol by boiling with water. The product is then crystallised from alcohol, and finally from chloroform, whereby the pure substance separates in long, silky needles, melting at 188°. It dissolves readily in warm chloroform, but is otherwise sparingly soluble in the usual solvents:

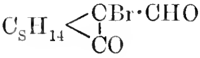
0·1515 gave 0·3470 CO_2 and 0·0690 H_2O. C = 62·47; H = 5·10.
$C_{21}H_{20}O_8$ requires C = 62·97; H = 5·04 per cent.

Neither salicylaldehyde nor the glucoside helicin reacts with pentaerythritol in presence of sulphuric acid; dextrose was also employed without result.

In view of the supposition that oxymethylenecamphor may under certain conditions undergo tautomeric change into the aldehydic form (Pope and Read, Trans., 1909, **95**, 171), the reaction was tried with this substance, but condensation was not effected. Claisen, Brühl, and Aschan (*Zeitsch. physikal. Chem.*, 1900, **34**, 60) agree that oxymethylenecamphor has the constitution (I), but that the bromo-derivative is a true aldehyde (II). Accordingly, the condensation was attempted with bromo-oxymethylenecamphor (*Ber.*, 1894, **27**, 2402), but again without success. In this connexion it is interesting to notice that each of these substances, if existing in the aldehydic form, would be similar in constitution to salicylaldehyde in possessing a hydroxyl group in the *a*-position with respect to the aldehyde group.


$$C_8H_{14}{<}\begin{matrix}C{:}CH{\cdot}OH\\ |\\ CO\end{matrix}$$

(I.)


$$C_8H_{14}{<}\begin{matrix}CBr{\cdot}CHO\\ |\\ CO\end{matrix}$$

(II.)

Dimethylenepentaerythritol, $C_5H_8O_4(CH_2)_2$, is prepared by warming a mixture of equal weights of pentaerythritol, 40 per cent. formaldehyde, and concentrated hydrochloric acid for one and a-half hours on the water-bath, and subsequent extraction with ether. It is very soluble, and melts at 50° (Schulz and Tollens, *loc. cit.*).

Acetaldehyde was treated in a similar manner, but in this case a tarry product was formed, which was not investigated further. By substituting 50 per cent. sulphuric acid for concentrated hydrochloric acid, the solution turned yellow, but there was no separation on cooling. After extracting the solution successively with ether and chloroform, and subsequently evaporating the solvent, nothing remained beyond a brown liquid, smelling strongly of the aldehyde; it thus appears that acetaldehyde does not react.

Chloral also failed to yield a condensation product when treated in a similar manner.

By warming glyoxal (10 grams) with 50 per cent. sulphuric acid (15 grams) and pentaerythritol (15 grams) for several hours on the water-bath, a gelatinous substance was produced. It was collected, washed repeatedly with hot water, and dried at 100°. The white, amorphous powder obtained in this way is quite insoluble in all the ordinary solvents; it is even unaffected by boiling nitrobenzene or phenol. It has no definite melting point, and thus exhibits all the characteristics of a substance of very high molecular weight:

0·1268 gave 0·2183 CO_2 and 0·0763 H_2O. C=46·95; H=6·75.
0·2430 ,, 0·4212 CO_2 ,, 0·1442 H_2O. C=47·27; H=6·64 per cent.

These results do not correspond with any simple condensation product; it is evident, however, that the pentaerythritol takes part in the reaction, since glyoxal heated alone with 50 per cent. sulphuric acid under similar conditions yields no such product.

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CCXX.—*The Electrochemistry of Solutions in Acetone. Part II. The Silver Nitrate Concentration Cell.*

By ALEXANDER ROSHDESTWENSKY and WILLIAM CUDMORE McCULLAGH LEWIS.

THE measurements here described are a continuation of those recently published by us (Trans., 1911, **99**, 2138) on the *E.M.F.*'s of a series of concentration cells, the solute being silver nitrate and the solvent acetone. In the present instance we have employed a much more sensitive capillary electrometer, one somewhat similar to the original Lipmann type. A glass tube 6 mm. in diameter contains a column of mercury 880 mm. in height, this column ending in a capillary which at the point of observation was 0·012 mm. in diameter. The capillary dipped into a solution of *N*/10-sulphuric acid. By means of this electrometer it was found that the acetone solutions could be measured to ±0·5 millivolt. The potentiometer method was employed as before, the Weston standard being taken as 1·0183 volts. The entire apparatus was carefully earthed.

The following table, which is self-explanatory, contains the results

TABLE I.

E.M.F. in Volts. Temperature 19°.

Concentration of $AgNO_3$.		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	Mean.
c_1 0·02*N*	c_2 0·01*N*	0·0110	0·0107	0·0105	0·0100	0·0120	0·0130	0·0130	—	—	—	—	0·0114
0·02	0·007	0·0190	0·0180	0·0200	0·0190	0·0220	0·0220	0·0216	0·0180	0·0190	0·0200	0·0200	0·0199
0·02	0·005	0·0280	—	—	—	0·0300	0·0290	0·0286	—	—	—	—	0·0289
0·02	0·0035	0·0360	0·0360	—	—	0·0350	0·0350	—	—	—	—	—	0·0355
0·02	0·002	0·0490	0·0490	—	—	0·0490	—	—	—	—	—	—	0·0490
0·02	0·001	(0·0584)	0·0595	0·0597	0·0599	(0·0673)	0·0653	0·0650	—	—	—	—	0·0621
0·01	0·007	0·0101	0·0100	0·0092	—	0·0080	0·0080	—	—	—	—	—	0·0090
0·01	0·005	0·0160	0·0156	—	—	0·0166	0·0150	0·0150	(0·0140)	—	—	—	0·0153
0·01	0·0035	0·0270	0·0268	—	—	(0·0250)	0·0260	0·0280	—	—	—	—	0·0265
0·01	0·002	0·0380	0·0380	0·0373	0·0390	0·0360	(0·0350)	(0·0356)	—	—	—	—	0·0369
0·01	0·001	0·0530	0·0520	—	—	0·0540	0·0540	0·0550	—	—	—	—	0·0536
0·007	0·005	0·0090	0·0085	—	—	0·0094	0·0090	—	—	—	—	—	0·0089
0·007	0·0035	0·0176	0·0173	—	—	0·0177	0·0168	0·0168	0·0168	0·0168	after 17	hours 0·0167	0·0171
0·007	0·002	0·0300	0·0303	—	—	0·0280	0·0270	—	—	—	—	—	0·0288
0·007	0·001	0·041	0·041	—	—	0·046	0·044	—	—	—	—	—	0·042
0·007	0·0005	0·055	0·056	—	—	—	—	—	—	—	—	—	0·0555

REMARKS.—The data of columns 1 and 2 refer to the same cell, readings being taken at an interval of 15 minutes. Columns 3 and 4 refer to cells refilled from same stock as that used for columns 1 and 2. Columns 5 to 11 refer to consecutive measurements at intervals of 15 minutes with different stock solutions from those used in Series 1 to 4.

of a series of concentration cells, the two solutions being placed in direct contact, so that the liquid|liquid potential difference is present as well as that of the electrodes.

Effect of Time on the Solutions.

A number of the solutions of silver nitrate in acetone were kept for six weeks in the dark, and at the end of that time concentration cells were set up exactly as in the foregoing experiments. The results are shown in table II.

TABLE II.

Temperature 19°.

Concentration of silver nitrate.				
c_1.	:	c_2.	*E.M.F.* in volts.	
0·01*N*		0·007*N*	0·0075	0·0080
0·01		0·005	0·0183	
0·01		0·0035	0·0266	
0·01		0·002	0·0380	
0·007		0·005	0·007	
0·007		0·0035	0·0183	
0·007		0·002	0·0288	0·0284

It will be noted that the values are, within the limit of error, nearly identical with those previously obtained, so that as far as *E.M.F.* measurements show, there is no change in the solutions with time.

E.M.F. *Measurements with Solutions Exposed to Light.*

The solutions employed for table I were each exposed for one day to sunlight, a small quantity of brown precipitate being thereby formed in the more concentrated liquids. The data obtained are given in the following table.

TABLE III.

Concentration of silver nitrate.			
c_1.	:	c_2.	*E.M.F.* in volts.
0·02*N*		0·01*N*	0·0105
0·02		0·007	0·020
0·02		0·0035	0·036
0·02		0·002	0·050
0·02		0·001	0·059
0·01		0·007	0·0092
0·01		0·005	0·016
0·01		0·0035	0·0269
0·01		0·002	0·037
0·01		0·001	0·052
0·007		0·005	0·008
0·007		0·0035	0·0168
0·007		0·002	0·030
0·007		0·001	0·041
0·007		0·0005	0·055

Exposure to light has, rather remarkably, had no measurable influence on the *E.M.F.* Any changes which may have taken place lie within the limits of experimental error.

Calculation of the Transport Number of the Anion of Silver Nitrate in Acetone.

As a result of earlier experiments it was concluded that solutions of silver nitrate in acetone behaved in accordance with simple osmotic theory, and that therefore Nernst's expressions for the *E.M.F.* of concentration cells were applicable. This was further verified by the following measurements made with cells having a solution of 0·01*N*-silver nitrate interposed as middle liquid.

Concentration of silver nitrate. c_1.	: c_2.	*E.M.F.* in volts.
0·007*N*	0·005*N*	0·010
0·007	0·0035	0·017

The mean values obtained when no middle liquid is interposed are 0·0089 and 0·0171 respectively (compare table I). The values are concordant within the limits of error. This should be the case if Nernst's formulæ are applicable.

Employing Jones's approximate value, namely, 0·62, for the transport number of NO_3' in silver nitrate, moderate agreement was obtained in our previous work between observed and calculated *E.M.F.*'s. We have therefore assumed the applicability of Nernst's formula for the *E.M.F.* of a concentration cell containing a liquid | liquid potential difference, and have used our more accurate *E.M.F.*

TABLE IV.

Concentration of silver nitrate.		*E.M.F.* observed (mean), volt.	*E.M.F.* calculated, assuming			Difference between observed and calculated values, neglecting bracketed numbers, millivolts.
c_1.	: c_2.		Transport number, $NO_3'=0·60$.	Transport number, $NO_3'=0·58$.	Transport number, $NO_3'=0·56$.	
0·02*N*	0·01*N*	0·0114	0·0103	0·0100	(0·0096)	+1·2
0·02	0·007	0·0199	0·0199	0·0193	(0·0186)	+0·3
0·02	0·005	0·0289	0·0288	(0·0279)	(0·0269)	+0·1
0·02	0·0035	0·0355	(0·0387)	(0·0374)	0·0361	−0·6
0·02	0·002	0·0490	—	—	0·0491	−0·1
0·02	0·001	0·0621	—	—	0·0642	−2·1
0·01	0·007	0·0090	—	—	0·0088	+0·2
0·01	0·005	0·0153	—	—	0·0157	−0·4
0·01	0·0035	0·0265	—	—	0·0264	+0·1
0·01	0·002	0·0369	—	—	0·0394	−2·5
0·01	0·001	0·0536	—	—	0·0544	−0·8
0·007	0·005	0·0089	—	—	0·0084	+0.5
0·007	0·0035	0·0171	—	—	0·0176	−0·5
0·007	0·002	0·0288	—	—	0·0305	−1·7
0·007	0·001	0·0420	—	—	0·0456	−3·6
0·007	0·0005	0·0555	—	—	0·0567	−1·2

results for the purpose of calculating the transport number which yields the best agreement between observed and calculated values. We have thus found that between the concentration limits 0·02—0·007 normal silver nitrate, the transport number of NO_3' lies between 0·60 and 0·58, the value of the transport number for more dilute solutions (to 0·0005*N*) being 0·56. The foregoing table shows the extent of the agreement obtained.

Further Attempts to Eliminate the Liquid|Liquid Potential Difference.

In the former paper we have shown that lithium nitrate interposed as the middle liquid cannot be used to annul the potential difference in that under the concentration conditions investigated it appears even to increase the existing potential. We have in the present instance investigated the effect of ammonium acetate as middle liquid. Its solubility was determined, and found to be 0·118*N* at 19°. This is considerably greater than that of other simple salts, such as potassium chloride or ammonium nitrate, which suggest themselves as suitable on other grounds, but is very much less than the concentrations of salts used to cut out the potential in the case of aqueous solutions. The theoretical basis for the process is, however, so vague, and the efficiency of the procedure even in the most favourable cases in aqueous solution by no means beyond question, that it seemed worth while to carry out a fairly comprehensive series of such measurements in the present instance. The results obtained are given in table V.

TABLE V.

Ammonium Acetate as Middle Liquid. E.M.F. *in Volts.*

Concentration of $AgNO_3$. c_1.	c_2	1.	2.	3.	4.	5.	6.	7.	Mean.
0·02*N*	0·01*N*	0·012	0·013	0·013	0·013	0·014	0·012	—	0·013
0·02	0·007	0·023	0·023	0·022	0·022	0·022	0·022	0·021	0·022
0 02	0·005	0·032	0·0314	0·032	0·032	—	—	—	0·032
0·02	0·0035	0·034	—	—	—	—	—	—	0·034
0·02	0·002	0·0515	0·0514	0·053	—	—	—	—	0·052
0·02	0·001	0·068	0·066	0·066	—	—	—	—	0·067
0·01	0·007	0·012	0·012	0·0115	0·0114	0·011	—	—	0·0116
0·01	0·005	0·016	0·015	0·0148	0·0152	0·020	0·0205	—	0·0169
0·01	0·0035	0·025	0·026	0·024	—	—	—	—	0·025
0·01	0·002	0·036	0·037	0·0397	0·0402	0·040	0·0397	—	0·039
0·01	0·001	0·054	0·0537	0·0537	0·0537	0·055	0·054	0·054	0·054
0·007	0·005	0·010	0·0008	0·0008	—	—	—	—	0·0009
0·007	0·0035	0·015	0·016	0·016	0·016	—	—	—	0·016
0·007	0·002	0·030	0·030	0·028	—	—	—	—	0·030
0·007	0·001	0·047	0·045	—	—	—	—	—	0·046

REMARKS.—Columns 1 and 2 refer to the same portion of solution. Columns 3 to 7 refer to a second portion of the solution.

A comparison of these values with those of table I show that the saturated ammonium acetate is without definite effect. In eleven cases the *E.M.F.* is increased to the extent of 2 or 3 millivolts; in three cases the *E.M.F.* is decreased. The results are therefore unsatisfactory, the increase in the *E.M.F.* in this case and with lithium nitrate standing in contradiction even to the direction of the effect anticipated.

It was observed that the solution of ammonium acetate in acetone darkened in colour markedly on exposure to the air and daylight. A series of measurements similar to those quoted in table V were therefore made, using ammonium acetate solutions which had been thus exposed for one day. No difference in the values of the *E.M.F.*'s could be detected. It is, of course, impossible to employ the ammonium acetate throughout the cell owing to the precipitation of sparingly soluble silver acetate. We have not succeeded, therefore, in eliminating the liquid|liquid potential difference.

It was found that other salts of silver, the chloride, cyanide, and acetate, were too sparingly soluble to allow of their being employed in concentration cells.

Summary.

(1) Employing a more sensitive form of capillary electrometer, further measurements have been carried out on the *E.M.F.* of concentration cells containing silver nitrate in acetone.

(2) Measurements were also carried out with solutions which had been exposed to sunlight for one day, as a result of which slight precipitation takes place, without, however, any measurable effect on the *E.M.F.*

(3) The *E.M.F.* of the concentration cells is unaffected by the interposition of a solution of silver nitrate of arbitrary concentration.

(4) On account of (3) and the results obtained in previous work, it was concluded that the Nernst formulæ are applicable. On this basis, the transport number of the anion of silver nitrate in acetone at 19° was calculated, namely, (0·60—0·58) for concentration limits 0·02*N*—0·007*N*, and 0·56 for lower concentrations.

(5) Attempts have been made to eliminate the liquid|liquid potential differences by the interposition of saturated ammonium acetate. In the majority of the cells examined, the *E.M.F.* is slightly raised. The validity of such "middle liquid" methods for acetone solutions at least is thus doubtful.

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CCXXI.—*The Influence of Neutral Solvents on Velocity of Reaction. Part II. Transformation of Anis*syn*aldoxime in Various Solvents.*

By Thomas Stewart Patterson and Harvey Hugh Montgomerie, M.A., B.Sc.

In a recent paper (this vol., p. 26) we described some experiments in which the influence of neutral solvents on the velocity of transformation of anis*syn*aldoxime into anis*anti*aldoxime was studied, the transformation being rendered apparent by a corresponding alteration in the rotation of ethyl tartrate used as an indicator. We have been able, earlier than we had expected, to extend these experiments to include other solvents, and give in the following pages an account of our work.

The method was briefly as follows: 15 c.c. of ethyl tartrate were delivered into a flask, and carefully weighed; 5 c.c. of the purified solvent were then added, and the weight of the mixture determined. This solution was divided into two approximately equal portions, both being weighed. To each was added as nearly as possible 4·76 per cent. by weight of *syn*oxime, recrystallised just previous to the experiment. These solutions were placed in a thermostat as soon as the oxime had dissolved, and readings of the rotation taken from time to time once a constant temperature of 26° had been reached. From the data obtained, the velocity of transformation of the *syn*oxime under these conditions may be calculated by the formula for a unimolecular reaction. For further details Part I. should be consulted, the present experiments having been carried out in exactly the same way as before.

The specimen of ethyl tartrate used was divided by distillation into two fractions, of which the first had $\alpha_D^{26} + 10·05°$ and the second $\alpha_D^{26} + 10·145°$. The rate of transformation of the oxime was first determined in each fraction alone.

Table I.

*Anis*syn*aldoxime in Ethyl Tartrate.*

	Number of Solution.	*p.*	*a.*	1000 *k.*	1000 *k.* (Mean of two Series.)
First fraction	I	3·85	2·38°	6·00	*6·08*
	II	3·85	2·38	6·16	
Second fraction	III	3·85	2·39	1·25	*1·257*
	IV	3·85	2·39	1·265	

For our purpose the first fraction was too rapid, and therefore the second was used. The difference in the constant demonstrates the presence of a catalytic agent which is quickly removed by distillation. The numbers obtained are contained in the following table.

TABLE II.

Neutral solvent.	Number of solution.	α.	1000 k.	1000 k. (Mean value.)
s-Tetrabromoethane	V	3·30°	11·02	
Pyridine	VI	0·77	5·59	*5·54*
	VII	0·78	5·48	
Aniline	VIII	1·70	55·6	*55·8*
	IX	1·70	55·13	
	X	2·34	56·62	
Dimethylaniline	XI	2·35	1·25	*1·27*
	XII	2·35	1·29	
Diphenylmethylamine	XIII	2·64	4·35	*4·38*
	XIV	2·64	4·41	
Diphenylamine	XV	2·40	7·37	*7·45*
	XVI	2·40	7·53	
Monomethylaniline	XVII	2·19	2·87	*2·89*
	XVIII	2·19	2·92	
Acetone	XIX	1·32	4·49	*4·43*
	XX	1·62	4·37	
Monomethylaniline .... (Specially purified)	XXI	2·19	3·21	*3·08*
	XXII	2·19	2·95	

Our previous work having shown that the velocity-constant for a sample of ethyl tartrate increases whilst a series of experiments is being performed, we finally determined the rate of change of the oxime in the ester alone. Three solutions were examined, all containing 3·85 per cent. of oxime. The total change was in each case 2·20°, the constants having the values 5·68, 5·33, and 5·58.

TABLE III.

Corrected Velocity of Transformation of Anissynaldoxime in Presence of Ethyl Tartrate and Various Solvents.

Added solvent.	Days elapsed since experiments commenced.	1000 k (observed).	1000 k (corrected).	1000 k (corrected and referred to 1·745).
None	0	1·26	1·26	1·745
s-Tetrabromoethane......	16	11·02	6·70	9·27
Pyridine	26	5·537	2·70	3·74
Aniline	29	55·36	25·52	35·33
Dimethylaniline	36	1·27	0·52	0·72
Diphenylmethylamine..	41	4·38	1·65	2·29
Diphenylamine	42	7·45	2·765	3·83
Monomethylaniline. I..	64	2·895	0·81	1·12
Acetone.....................	72	4·43	1·13	1·57
Monomethylaniline. II.	78	3·21	0·78	1·09
None	84	5·53	—	—

The mean value is 5·53, so that the constant for the specimen of ethyl tartrate had increased by a very considerable amount during the progress of the experiments. We therefore applied a correction to our results (see Part I., p. 33) on the assumptions that the increase of velocity which occurs in the homogeneous ester will occur in the same proportion in the solutions, and that it varies directly with elapsed time.

In the last column the corrected values for the constants are calculated to the number 1·745 as standard in order that they may the more easily be compared with the data given in Part I. The application of this correction alters very considerably, of course, the actual value of the constant, but it may be remarked that the sequence in columns 3 and 4 is almost unaffected, only acetone and diphenylamine changing places. The two values obtained for monomethylaniline agree closely when corrected, which justifies, to some extent, our method of correction. Nevertheless, on account of the large change which had taken place in the constant for the undiluted ethyl tartrate, we thought it desirable to repeat the whole series of experiments. In this case, however, we prepared a considerable quantity of ethyl tartrate, and distributed it among several glass tubes, which were then sealed off and kept in the dark, a fresh tube being opened for each experiment. This we found to be satisfactory, since the constant determined at the completion of our work was almost identical with that obtained at the commencement of the second series of experiments.

The results of the new observations are given in the following table:

TABLE IV.

Neutral solvent.	Number of solution.	Composition of solution.			*a.*	1000 k.	Mean 1000 k.
		E. T. :	*S.* :	*O.*			
None	XXVI	96·15	—	3·85	2·57°	1·07	*1·085*
	XXVII	96·15	—	3·85	2·57	1·08	
s-Tetrabromoethane	XXVIII	52·28	42·86	4·76	3·68	4·00	*3·94*
	XXIX	52·26	42·98	4·76	3·57	3·88	
Pyridine	XXX	74·61	20·61	4·76	1·19	1·30	*1·30*
	XXXI	74·63	20·63	4·76	1·19	1·30	
Aniline	XXXII	74·16	21·08	4·76	1·93	4·59	*4·71*
	XXXIII	74·16	21·08	4·76	1·85	4·83	
Diphenylmethylamine	XXXIV	73·71	21·62	4·77	2·74	0·63	*0·635*
	XXXV	73·67	21·56	4·76	2·74	0·64	
Monomethylaniline	XXXVI	74·62	20·62	4·76	2·18	0·35	*0·35*
	XXXVII	74·62	20·62	4·76	2·18	0·35	
Acetone	XXXVIII	77·54	17·70	4·76	1·79	0·57	*0·57*
	XXXIX	77·53	17·71	4·76	1·79	0·57	
Dimethylaniline	XL	74·83	20·41	4·76	2·36	0·20	*0·20*
	XLI	74·83	20·41	4·76	2·36	0·20	
Diphenylamine	XLII	72·16	23·08	4·76	2·42	1·64	*1·63*
	XLIII	72·14	23·10	4·76	2·42	1·62	
None	XLIV	96·15	—	3·85	2·57	1·10	*1·10*

Since the final result for the ethyl tartrate alone is so close to the original value it is not worth while to apply any correction. The numbers in the last column are reproduced in the second column of table V, and are calculated to the constant 1·745 in column three in order to allow of comparison with the corresponding data from the first series of experiments.

TABLE V.

*Velocity of Transformation of Anis*syn*aldoxime in Presence of Ethyl Tartrate and Various Neutral Solvents.*

	Series II.		Series I.	
Neutral solvent.	1000 k referred to 1·085.	1000 k referred to 1·745. A.	1000 k referred to 1·745. B.	Ratio, A/B.
s-Tetrabromoethane	3·94	6·392	9·27	1·21
Pyridine	1·30	2·109	3·74	1·74
Aniline........................	4 71	7·64	35·33	—
Monomethylaniline	0·35	0·57	1·10	1·89
Dimethylaniline............	0·20	0·32	0·72	2·25
Diphenylamine	1·63	2·64	3·83	1·45
Diphenylmethylamine ...	0·635	1·03	2·29	2·22
Acetone	0·57	0·92	1·57	1·70

From this table it will be seen that the sequence is identical in both series of experiments, although the actual constants are not the same. According to the assumptions we make in calculating our results to the standard constant 1·745—which, of course, is only standard to the extent that the ethyl tartrate we used in the experiments recorded in our first paper had this constant—the numbers in columns three and four should be the same, and our method is therefore faulty. The ratio of the numbers in columns three and four ought to be constant, and although this is not the case it seems clear that the value of the ratio varies irregularly about a mean. Another way of comparing the constants obtained in the two sets of experiments is to refer them to the smallest in each case as unit. Table VI is thus obtained.

TABLE VI.

Neutral solvent.	Series I.	Series II.
s-Tetrabromoethane	12·88	19·98
Pyridine	5·19	6·59
Aniline..............................	49·07	23·88
Monomethylaniline...............	1·53	1·78
Dimethylaniline	1·00	1·00
Diphenylamine	5·32	8·25
Diphenylmethylamine	3·18	3·22
Acetone..............................	2·18	2·88

Considering the character of our experiments, especially the facts that the total change we have to measure is less than 3° in every case except one, when it was about 3·5°, and also that the neutral solvent formed only about 25 per cent. by volume of the total solution, these numbers must be regarded as agreeing fairly well, except in the case of aniline. In our first series this reaction seems to have been greatly hastened in some manner that we are unable to explain.

We have already referred to the fact that the reaction in question is hastened by some catalyst contained in the ethyl tartrate, and we thought it very possible that this catalyst might be of an acid character produced in the preparation of the ester by the hydrochloric acid method. Since, however, the transformation takes place even faster in a fairly basic solvent like aniline, it seems improbable that the catalyst is acid. The difference between the constants for aniline and dimethylaniline is very great, and in our first series of experiments we thought this might be caused by the presence of dimethylaniline in our specimen of monomethylaniline, which, therefore, was purified by conversion into nitrosomethylaniline, this being reduced to monomethylaniline. The experiments with this pure sample, however, gave almost the same result as before (table III). It would appear, therefore, that in passing from aniline to monomethylaniline there is a very rapid fall in the value of the constant, the passage from mono- to di-methylaniline being accompanied by a much smaller change. That the influence of aniline cannot be attributed to its phenyl group may be inferred from the fact that in diphenylamine the transformation takes place much more slowly than in aniline, although more rapidly than in monomethylaniline, the introduction of another methyl group bringing about a further diminution of much the same magnitude as that observed in passing from mono- to di-methylaniline. It may be surmised that the reaction would take place very rapidly indeed in ammonia, the successive replacement of the hydrogen atoms of which by methyl, phenyl, or, presumably, other groups producing solvents of steadily diminishing influence on this transformation.

We chose some of these solvents with a view to discover whether any connexion could be traced between the influence of a solvent on the rotation of the ethyl tartrate used, and its influence on the velocity of transformation; thus *s*-tetrabromoethane has a very powerful effect in diminishing the rotation of dissolved ethyl tartrate, whilst aniline has a great influence of the opposite character. As appears, however, they resemble one another in hastening the transformation of the *syn*oxime. Again, pyridine which raises the rotation of the ester, has comparatively little effect on the oxime transformation, so that no connexion of the character suggested can be discovered from our data.

It is not possible to institute much comparison between these results and those of other, similar, investigations, since the solvents we have employed, with the exception of acetone, have mostly not been used in this way before, and in the case of acetone the data are so scanty that very little can be done with them meantime. If desired, some material will be found in table X (p. 34) of our previous paper.*

In the following table are collected the values found by us for all the solvents examined up to the present. They are calculated to an ethyl tartrate of constant 1·745, but it must be remembered that, having been arrived at with different samples of ester, the numbers must be regarded as approximate only.

Table VII.

Solvent.	1000 k referred to 1·745.	Solvent.	1000 k referred to 1·745.
Water	8·26	*p*-Xylene	2·44
Methyl alcohol	2·07	Mesitylene	2·13
Ethyl ,,	1·86	Nitrobenzene	2·94
n-Propyl ,,	1·69	Aniline	7·64
*iso*Butyl ,,	0·96	*s*-Tetrabromoethane	6·39
Allyl ,,	1·56	Diphenylamine	2·64
Benzyl ,,	3·14	Pyridine	2·11
Benzene	3·13	Diphenylmethylamine	1·03
Toluene	2·33	Acetone	0·92
o-Xylene	2·19	Monomethylaniline	0·57
m-Xylene	2·34	Dimethylaniline	0·32

The experiments recorded here were carried out by the use of a large polarimeter kindly placed at our disposal by the Carnegie Trustees for the Universities of Scotland, to whom we have pleasure in expressing our thanks.

Organic Chemistry Department,
University of Glasgow.

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* In Part I (p. 38), when discussing Dimroth's application of van't Hoff's suggestion correlating the velocity of transformation of a labile substance in various media with its solubility in these media, we remarked that "the solubilities found by Dimroth, *which probably, from the method of determination, are really those of the liquid solute,* show a remarkable relationship to the values found for the velocity constant (*Annalen*, 1910, **377**, 131)." We had, however, overlooked the fact that the two sets of solubility determinations quoted by Dimroth were carried out by different methods and that our comment (italicised above) does not apply to the set to which we were referring.

CCXXII.—*Organic Derivatives of Silicon. Part XV. The Nomenclature of Organic Silicon Compounds.*

By Frederic Stanley Kipping.

Up to the present time the nomenclature of organic derivatives of silicon has not received much attention, and the names given to such compounds have been chosen rather at random. The principal suggestion which, so far, has been made in order to systematise the nomenclature is that silicon hydride should be called *silicane* (Kipping, Trans., 1907, **91**, 209); the immediate derivatives of this compound may then receive names corresponding with those of analogous derivatives of methane.

The term *silicyl* has also been used to denote the univalent radicle $\cdot SiH_3$, which corresponds with the methyl group; compounds such as $SiPh_3Cl$ and $SiPhEtPrCl$, for example, have been named triphenylsilicyl chloride and phenylethylpropylsilicyl chloride respectively.

It now seems desirable to make some further suggestions in order that the substances described in the following communications may be named in accordance with some definite system.

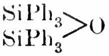
It is therefore proposed that the names silicane and silicyl should be retained, and that the hydroxy-derivatives of silicane should be called silicanol, silicanediol, etc., as illustrated by the following examples:

$SiH_3{\cdot}OH$	$SiPh_3{\cdot}OH$	$SiH_2(OH)_2$	$SiPh_2(OH)_2$
Silicanol.	Triphenylsilicanol.	Silicanediol.	Diphenylsilicanediol.

The term *silicone* has already been used to denote the analogues of the ketones, and may be advantageously retained for this purpose, in which case the following compounds would be named as shown below:

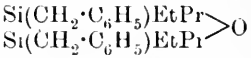
$SiEt_2O$	$SiPh_2O$
Diethylsilicone.	Diphenylsilicone.

The great dissimilarity between the ethers and silicon compounds of a corresponding type, containing the group $\begin{matrix}Si\\Si\end{matrix}{>}O$, led the author to suggest that the latter should be termed oxides (Trans., 1907, **91**, 726); in accordance with this suggestion, compounds which may be regarded as derived from silicanol, with loss of the elements of water, have been named as illustrated by the following examples:



$$\begin{matrix}SiPh_3\\SiPh_3\end{matrix}{>}O$$

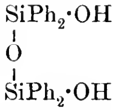
Triphenylsilicyl oxide.



$$\begin{matrix}Si(CH_2{\cdot}C_6H_5)EtPr\\Si(CH_2{\cdot}C_6H_5)EtPr\end{matrix}{>}O$$

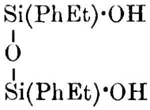
Benzylethylpropylsilicyl oxide.

The nomenclature of the more complex substances, which may be derived from two or more molecules of silicanediol, presents some difficulty, but as such compounds have now been obtained, the matter must be considered. It is therefore proposed that, for these substances, such names should be chosen as would show how many molecules of the silicanediol have condensed together, and how many molecules of water have been eliminated in the process. The following examples may serve to illustrate this suggestion:



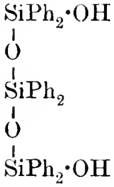
$$\begin{array}{l}SiPh_2\cdot OH\\ |\\ O\\ |\\ SiPh_2\cdot OH\end{array}$$

Anhydrobisdiphenylsilicanediol.



$$\begin{array}{l}Si(PhEt)\cdot OH\\ |\\ O\\ |\\ Si(PhEt)\cdot OH\end{array}$$

Anhydrobisphenylethylsilicanediol.

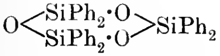


$$\begin{array}{l}SiPh_2\cdot OH\\ |\\ O\\ |\\ SiPh_2\\ |\\ O\\ |\\ SiPh_2\cdot OH\end{array}$$

Dianhydrotrisdiphenylsilicanediol.

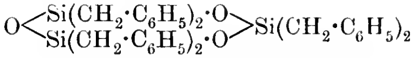
It will be seen that the names of such condensation products are rather long; on the other hand, they have the advantage of indicating the constitutions of the compounds which they respectively represent.

The "multimolecular silicones" derived from these condensation products by the further loss of the elements of water could then be named in accordance with a similar plan, the name showing how many molecules of the silicanediol had condensed together and how many molecules of water had been eliminated in the process; the following examples serve as illustrations.



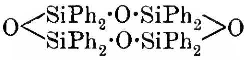
$$O{<}\begin{array}{l}SiPh_2\cdot O\\ SiPh_2\cdot O\end{array}{>}SiPh_2$$

Trianhydrotrisdiphenylsilicanediol.



$$O{<}\begin{array}{l}Si(CH_2\cdot C_6H_5)_2\cdot O\\ Si(CH_2\cdot C_6H_5)_2\cdot O\end{array}{>}Si(CH_2\cdot C_6H_5)_2$$

Trianhydrotrisdibenzylsilicanediol.



$$O{<}\begin{array}{l}SiPh_2\cdot O\cdot SiPh_2\\ SiPh_2\cdot O\cdot SiPh_2\end{array}{>}O$$

Tetra-anhydrotetrakisdiphenylsilicanediol.

University College,
Nottingham.

CCXXIII.—*Organic Derivatives of Silicon. Part XVI. The Preparation and Properties of Diphenylsilicanediol.*

By Frederic Stanley Kipping.

The primary object of this research was to ascertain the relation between the two dibenzyl compounds of the composition $C_{14}H_{16}SiO_2$, which had been obtained by Robison and Kipping (Trans., 1908, **93**, 439) by the hydrolysis of dichlorodibenzylsilicane (dibenzylsilicon dichloride). For this purpose a comparative study of the products of hydrolysis of dichlorodiphenylsilicane seemed to be desirable.

At that time, one such product, namely, diphenylsilicanediol ("diphenylsilicol"), had already been described by Dilthey and Eduardoff (*Ber.*, 1904, **37**, 1139), who obtained it by decomposing highly impure dichlorodiphenylsilicane with water; they described it as crystallising from benzene in needles, which melted at 138—139°. Quite recently the results of an investigation of "dibenzylsilicol" and "diphenylsilicol" have been published by Martin (*Ber.*, 1912, **45**, 403).*

In the experiments described in this paper, dichlorodiphenylsilicane was prepared by the interaction of silicon tetrachloride and magnesium phenyl bromide, and the pure compound was decomposed with water, ammonium hydroxide solution, or a dilute solution of potassium hydroxide. At first consideration it might not seem to be a very difficult task to hydrolyse the dichloro-

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* The examination of the dibenzyl compounds, referred to above, having been left unfinished, owing to the departure from Nottingham of Dr. Robison, I continued the work in conjunction with Dr. Martin, with whom I also resumed the study of diphenylsilicanediol. After many months of strenuous application, Dr. Martin came to the conclusion that he had obtained two isomeric "diphenylsilicols," and had also devised methods for their conversion one into the other, but before the research was really finished he was obliged to abandon it, in order to take up an appointment elsewhere. On his departure, Dr. Martin handed to me a record of his work, which, a short time afterwards, I began to consider, with a view to the publication of a joint paper. As some of the statements in this record seemed to me to require verification, I repeated some of Dr. Martin's more important experiments; having failed to confirm them, I informed him of the results of my observations and that I thought it necessary to revise the whole of the work before sending the paper to be published. After some discussion, it was finally left to him to decide whether or not he should communicate his own results under his own name; his decision led to the publication of the paper referred to above, in which, unfortunately, as will be shown later, he gave a very erroneous account of diphenylsilicanediol.

derivative by these processes, and to isolate the compound which had been formed, and yet the task proved to be an exceptionally troublesome one.

Although it was easy enough to obtain a crystalline product, different preparations varied greatly in their behaviour, and under certain conditions were so readily changed that the results were most perplexing; some preparations, for example, when warmed with solvents, were converted into viscid, glue-like products; some of these glues were readily soluble in alcohol, others almost insoluble. A further difficulty was due to the fact that the preparations did not melt, but decomposed with effervescence, when they were heated, and although they liquefied in this process, the temperature at which decomposition occurred varied very greatly with different preparations, even after they had been recrystallised.

As illustrations of the behaviour here outlined, the following summary of the results of hydrolysing the dichloride under different conditions may be given, accompanied by the statement that pure diphenylsilicanediol usually decomposes at about 128—132°, and is readily and completely soluble in a 5 per cent. aqueous solution of potassium hydroxide.

The decomposition of dichlorodiphenylsilicane with cold water results in the formation of a crystalline solid, which contains a large proportion of the dihydroxy-compound; after having been washed with cold chloroform, which extracts an oily mixture of at least three substances, this product begins to liquefy and decompose at about 145—150°; but liquefaction is not complete until the temperature has risen to about 165°. When the washed preparation is heated with solvents in order to crystallise it, it may be completely converted into an oil, which is readily soluble in alcohol, or it may give crystalline deposits, which vary considerably in decomposition point; all such deposits are impure, as they do not dissolve completely in a 5 per cent. aqueous solution of potassium hydroxide, and the impurity is not eliminated by recrystallisation from various anhydrous solvents.

The decomposition of dichlorodiphenylsilicane with excess of a concentrated solution of ammonium hydroxide results in the formation of a viscid oil, which is practically free from diphenylsilicanediol, and is a mixture of at least three compounds.

The hydrolysis of the dichloride with excess of a 5 per cent. aqueous solution of potassium hydroxide results in the production of a clear solution of the potassium derivative, $SiPh_2(OK)_2$ or $SiPh(OH)\cdot OK$; from this solution, diphenylsilicanediol is precipitated on the addition of acids or certain salts, but the properties of the precipitate vary very considerably with the nature and the quantity of the precipitant.

When the alkaline solution is just neutralised with acetic acid, the air-dried precipitate almost invariably decomposes, and liquefies completely at about 105—110°, and when heated with solvents, such as ether or ethyl acetate, it may be completely converted into a glue-like substance, which is practically insoluble in alcohol. It may be recrystallised from various solvents in the cold, and thus obtained in colourless anhydrous needles, decomposing at about 115°, but the decomposition point of such preparations often rises to about 140° when the specimens are merely kept for a short time at the ordinary temperature. When ammonium chloride, or a considerable excess of hydrochloric acid, is used to precipitate the diphenylsilicanediol from its alkaline solution, the air-dried precipitate liquefies with effervescence at about 145—155°; such precipitates may be recrystallised from hot solvents without their undergoing much observable decomposition, but even then they are invariably heterogeneous, and leave an insoluble residue when they are treated with a 5 per cent. aqueous solution of potassium hydroxide.

Observations such as those summarised above, the undoubted existence of the two dibenzyl compounds of the composition $C_{14}H_{16}SiO_2$ described by Robison and Kipping (*loc. cit.*), and the statement in Martin's record that he had isolated two isomeric forms of diphenylsilicanediol, decomposing at 140° and 160° respectively, all seemed to point in the one direction, and many attempts were made to isolate the two or more compounds, which were presumably contained in the above preparations.

In the course of these attempts it was found that the diphenylsilicanediol, precipitated from its alkaline solution with acetic acid, could be obtained in an apparently pure condition in colourless prisms, which were completely soluble in a 5 per cent. potassium hydroxide solution, and decomposed with effervescence at 115—118°; on the other hand, the compound, precipitated with excess of hydrochloric acid, was also obtained in needles, which, in spite of the fact that they were not quite pure, and were not completely soluble in potassium hydroxide solution, did not decompose and liquefy until about 140—145°.

As various specimens of the preparations, decomposing at 115—118°, gave on analysis results agreeing well with those required for a diphenylsilicanediol, it had to be assumed provisionally that they represented an isomeride or a polymeride of the compound, $SiPh_2(OH)_2$, described by Dilthey and Eduardoff as melting at 138—139°, and also of that described by Martin as decomposing at about 160°. It was further observed that the preparations decomposing at 115—118° were transformed into those having the higher decomposition point when they were recrystallised from cold solvents in the presence of a mere trace of hydrochloric acid; this fact, of course, was compatible with the view that the acid had brought about some isomeric or polymeric change.

There was, however, apart from all theoretical considerations, one experimental difficulty which, obviously, had to be overcome before a definite conclusion could be reached, namely, the removal from the preparations decomposing at temperatures above 140° of the small proportion of impurity, which was insoluble in potassium hydroxide solution. It certainly did not seem very probable that these recognisably impure preparations could be an impure form of the apparently pure substance decomposing at 115—118°, but it was a possibility which had to be considered, and which could only be decided by eliminating the impurity. For this purpose the preparations in question were systematically fractionally crystallised from various anhydrous solvents and various mixtures of such solvents, but the results were most unsatisfactory; although the deposits were well crystallised, and, as a rule, appeared homogeneous, they invariably retained impurity, as shown by their behaviour towards potassium hydroxide solution; moreover, the decomposition points of the various fractions were most irregular, and ranged from about 140° to 165°.

It was ultimately discovered that by the use of aqueous acetone and chloroform alternately, in the manner described later (p. 2121), the impurities in all such fractions could be removed, and that the pure diphenylsilicanediol which was thus obtained (usually) liquefied completely at 128—132°.

By the same method of purification, diphenylsilicanediol was also isolated from those apparently pure preparations which liquefied completely at about 118°.

The impurity which was thus removed from any preparation was relatively small in quantity, and consisted as a rule of an oily mixture of several compounds; as this mixture was readily soluble in ether, ethyl acetate, and other anhydrous solvents, and yet was not removed when the impure diphenylsilicanediol was recrystallised repeatedly from these solvents, it would seem that the impurities of which the mixture was composed had been adsorbed by the crystals of the diol.

Whatever may be the cause of the great difficulty of separating diphenylsilicanediol from relatively small quantities of certain soluble impurities, innumerable observations have shown that all those specimens of the diol which contain an appreciable proportion of the substances insoluble in a 5 per cent. aqueous solution of potassium hydroxide, invariably decompose at a much higher temperature than 128—132°, sometimes not until about 165°; pure specimens of diphenylsilicanediol, on the other hand, as stated above, usually decompose and liquefy completely below 132°, although very occasionally the decomposition does not occur until the temperature has been raised to about 160°.

This irregular and unusual behaviour, in the author's opinion, is not due to the existence of an isomeride of the compound $(C_6H_5)_2Si(OH)_2$, to which, indeed, it would be difficult to assign a structural formula, but is to be explained as follows: The crystalline form of diphenylsilicanediol, which separates from solvents at temperatures within the limits of those employed (about 10—60°), decomposes and liquefies completely at about 128—132°; but when near its decomposition point, this form, *A*, is in a metastable condition, and may change into another crystalline modification, *B*, which only decomposes at much higher temperatures, namely, at about 160°. The pure compound, as a rule, decomposes before the change in crystalline form occurs; in presence, however, of a sufficiently large proportion of those substances which are insoluble in a 5 per cent. aqueous solution of potassium hydroxide, its partial or complete transformation into the crystalline form of higher decomposition point invariably takes place, probably because one or more of these impurities is isomorphous with this form, *B*.

Whether this suggested explanation of the observations is true in all particulars or not, there does not seem to be any evidence of the existence of the isomeric diphenylsilicanediols described by Martin, and judging from the methods of preparation and decomposing points of his supposed isomerides, both must be regarded as impure specimens of the diol. In justice to Martin, however, it should, perhaps, be pointed out, that not only was he misled by a presumed analogy between dibenzylsilicanediol and diphenylsilicanediol, which, in fact, did not exist, but that the difficulties presented by the investigation of the last-named compound were altogether exceptional, and might have led into error a much more experienced chemist.

The results of further experiments on diphenylsilicanediol, which are described later, elucidate many of the observations which are recorded in this paper. For the sake of clearness it may be briefly stated here that diphenylsilicanediol is very readily decomposed by traces of alkalis, and also, but not so readily, by traces of acids, giving compounds which in their turn are further changed by these same reagents; consequently, the product obtained from the dichloride by the various methods indicated above may contain variable quantities of impurities, the nature of which depends on its method of preparation and subsequent treatment; further, unless the product is completely freed from alkali or acid before it is heated with solvents, it may be completely decomposed and converted into oily or glue-like mixtures.

EXPERIMENTAL.

Preparation of Dichlorodiphenylsilicane, $SiPh_2Cl_2$.

The action of different quantities of magnesium phenyl bromide on silicon tetrachloride was studied by Dilthey and Eduardoff (*loc. cit.*), who found that the product always consisted of a mixture, even when molecular proportions of the materials were employed; they described their methods for the preparation of chlorotriphenylsilicane and dichlorodiphenylsilicane, but they did not isolate these compounds; they hydrolysed their crude reaction mixtures with ice-cold water, and then purified the products of hydrolysis.

The author's observations confirm those of Dilthey and Eduardoff that the above interaction gives a mixture, no matter what proportions of magnesium phenyl bromide are used; nevertheless, with a suitable quantity of the Grignard reagent, a fairly satisfactory yield of diphenyldichlorosilicane can be obtained.

The following method was employed: Silicon tetrachloride (170 grams) is cooled to 0° in a flask, provided with a stirrer, and a carefully prepared ethereal solution of magnesium phenyl bromide ($2\frac{1}{4}$ mols.) is slowly added in the course of about one and a-half hours. The contents of the flask are then left at the ordinary temperature during about twelve hours; it is advisable to shake the flask vigorously at intervals during this time, otherwise the magnesium salt, as it separates, may form a solid cake, which cannot afterwards be removed. The flask is next heated during about three hours on a reflux apparatus; this is a very necessary operation, as the interaction is not complete at the ordinary temperature, and, moreover, the magnesium salt is still in a gelatinous condition, and, at this stage, cannot be easily separated by filtration. The ethereal solution of the silicon compounds is then filtered from the crystalline magnesium salt in absence of moisture (compare Kipping, Trans., 1907, **91**, 216), the residue is washed with pure ether, and the combined filtrate and washings are evaporated on the water-bath; towards the end of this operation a further quantity of magnesium salt is almost invariably deposited, and the separation gradually increases when the oily mixture is heated on the water-bath during about half an hour. It would seem, therefore, either that the magnesium salt at first remains dissolved in the ethereal solution, or that the reaction is not complete, even after the ethereal solution has been boiled during about three hours. In consequence of this separation of magnesium salt, the oily product must again be filtered and the residue washed with ether.

The clear, brownish-yellow oil is distilled from an ordinary distillation flask, under a pressure of 50 mm. After traces of ether and bromobenzene have passed over, the thermometer rises and remains for some time in the neighbourhood of 110—120°, and the fraction collected between these temperatures consists principally of trichlorophenylsilicane; the thermometer then rises rapidly to about 190°, and a very large fraction, consisting principally of dichlorodiphenylsilicane, is collected between this temperature and about 225°. Another rapid rise then occurs, and the fractions collected from about 260—300° deposit crystals of chlorotriphenylsilicane in the course of some hours. Above 300° little distils, but there remains in the flask a considerable quantity of a very viscid, black oil. The various fractions are systematically redistilled, those containing the diphenyl compound preferably under diminished pressure; in this way, from 170 grams of silicon tetrachloride there are ultimately obtained about 30 grams of trichlorophenylsilicane, boiling at 197—202° (atmospheric pressure), about 110 grams of dichlorodiphenylsilicane, boiling at 200—210°/45 mm., and about 15 grams of crystalline chlorotriphenylsilicane, together with smaller quantities of mixtures of these compounds, and possibly a little diphenyl.

The dichlorodiphenylsilicane boiling at about 200—210°/45 mm. generally contains a very small proportion of diphenyl, but for most purposes this is of no consequence. When further purified, the dichloride is obtained as a colourless liquid, boiling at 202—204°/45 mm., which fumes slightly in moist air; a sample of such a preparation was analysed, with the following result:

0·7414 gave 0·8443 AgCl. Cl = 28·14.

$C_{12}H_{10}Cl_2Si$ requires Cl = 27·9 per cent.

Decomposition of Dichlorodiphenylsilicane with Water.

Dichlorodiphenylsilicane is readily decomposed by cold water, with development of heat. In preparing the dihydroxy-compound by this method, the oily dichloride was slowly dropped into a large volume of water, which was vigorously stirred and cooled during the whole operation. The somewhat pasty solid was washed with water and dried in the air. It was first extracted with warm light petroleum to remove any diphenyl which might be present, and then with cold chloroform, which dissolved a considerable quantity of a pale yellow oil. The perfectly colourless, crystalline residue thus obtained usually began to sinter at about 150°, but did not liquefy completely until about 165°. When treated with various solvents, such as ether, ethyl acetate, acetone, etc., it sometimes gave orange-yellow solutions, which, however, gave colourless deposits when they were completely evaporated at the ordinary temperature. These colourless deposits again gave the coloured solutions, and so on.

Some preparations were completely or partly converted into oily products when attempts were made to recrystallise them from hot solvents, such as ether or ethyl acetate. This behaviour was doubtless due to the presence of traces of hydrochloric acid, which had been retained when the pasty solid was washed with water. Other preparations separated from hot ethyl acetate, etc., in colourless needles, and were fractionally crystallised; although the various fractions appeared to be homogeneous and identical, they decomposed at different temperatures, the most sparingly soluble at about 158—165°, the most readily soluble at about 140—150°. All the fractions were impure, and left a residue when they were treated with a 5 per cent. aqueous solution of potassium hydroxide, the most sparingly soluble portion giving the largest quantity of insoluble matter. From these impure, although repeatedly recrystallised specimens, pure diphenylsilicanediol was finally isolated by the method described later (p. 2121).

Decomposition of Dichlorodiphenylsilicane with Ammonium Hydroxide Solution.

As it seemed to be probable that the impurities contained in the diphenylsilicanediol, prepared by the foregoing method, were produced by the action of the hydrochloric acid on the original product of hydrolysis, experiments were made on the decomposition of the dichloride with a cold concentrated solution of ammonium hydroxide. The results, however, were most unsatisfactory.

When the dichloride was slowly dropped into a well-stirred solution of ammonium hydroxide, it was completely converted into a pale yellow oil, which after having been extracted with cold light petroleum and thus freed from traces of diphenyl, remained liquid during many weeks. This oil was soluble in alcohol; it did not contain any appreciable proportion of diphenylsilicanediol, because, when treated with a 5 per cent. aqueous solution of potassium hydroxide, it gave an extract from which acids precipitated only small quantities of the dihydroxy-compound.

The further investigation of this oil will be described in the following paper.

Decomposition of Dichlorodiphenylsilicane with a Solution of Potassium Hydroxide.

At an early stage of this investigation it was observed that the crude diphenylsilicanediol, precipitated from a solution of its potassium derivative with dilute acetic acid, had a much lower decomposition point than specimens obtained by precipitation with hydrochloric acid, and generally contained a relatively small quantity of matter which was insoluble in potassium hydroxide solution; as this observation seemed to confirm the conclusion that the dihydroxy-compound was changed by hydrochloric acid, the following method of preparation was tried. Dichlorodiphenylsilicane (1 mol.) was slowly dropped into a 5 per cent. aqueous solution of potassium hydroxide (more than 4 mols.); as a slight development of heat occurred, the solution was cooled with water and well stirred during the operation.

The pure dichloride gave a clear, colourless solution of the potassium derivative, but unless the dichloro-compound had been very carefully fractionated, it contained traces of diphenyl, which remained suspended in the alkaline solution and necessitated filtration. During this operation the solution and the filtrate nearly always became turbid, owing to the absorption of atmospheric carbon dioxide, and it was very necessary to carry out the operation as quickly as possible, because the turbidity was difficult to remove by further filtration.

When the clear alkaline solution was cautiously neutralised, or rendered very slightly acid, with acetic acid, it gave a somewhat gelatinous precipitate, which was so bulky that the mixture became a thick, white paste; the precipitate, which under the microscope appeared to consist of amorphous particles, was readily separated by filtration and washed with water by the aid of the pump, but even when it had been well pressed and left on porous earthenware during some hours, it retained an extraordinarily large proportion of water. The freshly precipitated substance was readily and completely dissolved by a 5 per cent. solution of potassium hydroxide, but, as a rule, it changed so quickly that by the time it had been washed, it was no longer completely soluble.

A great many different samples of air-dried preparations obtained in the above manner were examined; when heated slowly from the ordinary temperature, they all began to decompose at about 105°, and at about 107—110° they had completely liquefied, effervescence taking place owing to the escape of steam. Some air-dried preparations, which were heated at 100°, decomposed and liquefied completely in the course of ten to twenty minutes.

When attempts were made to purify the precipitated diphenylsilicanediol by recrystallisation, it behaved in a very curious manner. On being warmed with solvents such as ether, ethyl acetate, etc., it seemed as a rule to be completely decomposed, and on subsequent evaporation at the ordinary temperature, the solutions gave a viscid, oily residue, which was very sparingly soluble in alcohol. When dissolved in these solvents at the ordinary temperature it was sometimes deposited, by the spontaneous evaporation of the solutions, as a lustrous powder, which liquefied at about 140—155°; at other times the solutions gave crusts of ill-defined prisms, whilst a considerable proportion of oily matter (readily soluble in chloroform) remained in the mother liquor. These crusts usually decomposed with effervescence, and liquefied completely at about 113—115°, but even when well washed with chloroform they still retained some impurity which was insoluble in a 5 per cent. potassium hydroxide solution. If such partly purified preparations were recrystallised from cold ether or ethyl acetate, colourless needles, decomposing at about 113—115°, might be obtained; on the other hand, the decomposition point of the needles might suddenly rise to about 135—140°.

This change in properties was apparently not due to the removal of some impurity in the mother liquor, because a given sample, repeatedly dissolved in cold ether, nearly always changed, sometimes after the first, sometimes after the second or third operation, even when the solvent was completely evaporated each time. It was also observed that those preparations, which decomposed at 113—115°, sometimes changed spontaneously in the course of a few hours at the ordinary temperature; they became white and opaque, and in such cases the decomposition point was found to have risen to about 138—145°.

In spite of the fact that some preparations changed, apparently spontaneously, at the ordinary temperature, it was sometimes possible to recrystallise small quantities of material from hot ethyl acetate or chloroform without any rise in decomposition point taking place; the first time, in fact, that a preparation of this low decomposition point was obtained, no sign of instability was observed and no special precautions were taken in its purification, and yet it was obtained in fairly large prisms liquefying at about 116°.

As the addition of a trace of hydrochloric acid to a solution of these preparations invariably brought about a rise in decomposition point to about 145°, it seemed possible that the behaviour just referred to might be due to the presence of traces of acids in the solvents employed. Some specimens were therefore recrystallised from ether at the ordinary temperature, the ethereal solution resting on water which contained a trace of potassium hydroxide; in these circumstances the diphenylsilicanediol was deposited in beautiful, lustrous prisms, which were completely soluble in potassium hydroxide solution, and decomposed with effervescence at 115—118°. Similar results were obtained when the preparations were recrystallised from ether in presence of a trace of piperidine, but neither method gave very satisfactory results, as, unless the operation was conducted quickly, the diphenylsilicanediol was decomposed.

A very simple modification in the method of obtaining diphenylsilicanediol from its alkaline solution seemed to give a pure preparation, or, at any rate, one which was completely soluble in potassium hydroxide solution; this was the addition of a little ether to the solution of the potassium salt before precipitating with acetic acid. In presence of the ether, the precipitate lost entirely its gelatinous character; it was far less bulky, quite distinctly crystalline, and was readily freed from water when it was pressed on porous earthenware. As such preparations appeared to be homogeneous under the microscope, were completely soluble in potassium hydroxide, and had the same decomposition point as the prisms obtained from ether, they seemed to be pure diphenylsilicanediol.

The following analyses of three different air-dried specimens agreed with this view:

I. 0·1454 gave 0·3554 CO_2 and 0·0750 H_2O. C = 66·7; H = 5·7.
II. 0·1610 ,, 0·3932 CO_2 ,, 0·0838 H_2O. C = 66·6; H = 5·8.
0·1956 ,, 0·0547 SiO_2. Si = 13·2.
III. 0·1743 ,, 0·4254 CO_2 and 0·0885 H_2O. C = 66·6; H = 5·6.
0·1489 ,, 0·0419 SiO_2. Si = 13·2.

$C_{12}H_{12}O_2Si$ requires C = 66·6; H = 5·6; Si = 13·1 per cent.

Notwithstanding this evidence, there is little doubt that these samples contained a small proportion of impurity, which lowered the decomposing point of the diol, but which could be removed by the method given later.

It would seem from subsequent observations that the behaviour of the diphenylsilicanediol, precipitated with acetic acid as described above, is due to the presence of traces of potassium hydroxide which are adsorbed from the alkaline solution by the somewhat gelatinous precipitate, and are not removed when the solution appears to be neutralised, or when the precipitate is subsequently washed with water; as a result of the action of the alkali, small quantities of products, some of which are insoluble in potassium hydroxide, are formed, and, by the continued action of the alkali before or after recrystallisation, these products may be further changed, and even the whole of the diphenylsilicanediol may be decomposed. When precipitation occurs in presence of ether, the precipitate is not colloidal, and does not adsorb alkali, or does so to a limited extent only, in consequence of which it is far more stable; such precipitates, however, contain a small proportion of impurity, which is soluble in solutions of alkali hydroxides.

Precipitation of Diphenylsilicanediol with Hydrochloric Acid.

When a solution of diphenylsilicanediol in potassium hydroxide was treated with hydrochloric acid, it gave a bulky precipitate, which seemed to have much the same gelatinous character as that obtained with acetic acid, but which, when air-dried, had a much higher decomposition point than the latter; the decomposition point, moreover, seemed to vary with the quantity and concentration of the acid which was used, and with the time which elapsed before the precipitate was separated and washed. If, for example, the solution was only just neutralised, and the precipitate was immediately separated, the decomposition point of the air-dried sample might be 130—135°; if, however, the solution was strongly acidified and the precipitate was not separated until the next day, the sample might only sinter slightly at about 140°, and not liquefy until about 160—165°. Such preparations, especially those which had remained for some time in contact with hydrochloric acid, contained a variable quantity of matter which was readily soluble in cold chloroform; when this had been extracted and the residue was fractionally crystallised from ether, ethyl acetate, acetone, etc., deposits, which decomposed from 160° to 170°, or from 135° to 145°, or at intermediate temperatures, were obtained. All these fractions appeared homogeneous, but left a variable quantity of an insoluble residue when treated with a 5 per cent. potassium hydroxide solution.

Repeated attempts were made to obtain from them a pure sample of the diol, but fractional crystallisation from the different media already mentioned did not give the desired result. During these experiments it was noticed that when solutions in ether or ethyl acetate were evaporated on the water-bath, crystallisation did not take place, even when the solutions had become highly supersaturated, but when such solutions were then cooled, they gave either a transparent gelatinous mass or a cotton-wool-like solid, which then gradually changed to a crystalline powder.

Preparations apparently very similar in character to those just described, but nearly free from matter soluble in cold chloroform, were obtained when alkaline solutions of the diol were treated with excess of ammonium chloride, which precipitated the whole of the diphenyl compound; the fractional crystallisation of these preparations failed to give a product which was completely soluble in potassium hydroxide solution, and the decomposition points of the well crystallised fractions varied from about 135 to 160°.

Isolation of Diphenylsilicanediol.

In the course of the experiments recorded above there had accumulated a considerable quantity of recrystallised, impure diol, which had been produced by the decomposition of the dichloride with water, or from the potassium derivative of the diol, by precipitation with hydrochloric acid or ammonium chloride. Different samples or fractions of this material showed very considerable differences in decomposition point, some liquefying at about 130—140°, others at 140—150°, or even up to 160°. Preparations of an apparently similar character had also been obtained from those decomposing at about 115°; when the latter were dissolved in ethyl acetate with the addition of a trace of hydrochloric acid, the solutions gave on spontaneous evaporation colourless needles or prisms, decomposing from about 145° up to 160°.

Many of these samples had been repeatedly fractionally crystallised from ethyl acetate, ether, acetone, benzene, etc., and from mixtures of chloroform and ether, and chloroform and acetone, but in no case had a pure preparation been obtained; although the crystals which separated from warm solvents consisted of beautiful, lustrous needles or prisms, and appeared homogeneous, they invariably left an insoluble residue when treated with potassium hydroxide solution. The deposits obtained by the spontaneous evaporation of the solutions occasionally appeared to be heterogeneous, and consisted of lustrous needles, together with white, cauliflower-like masses, which crept up and over the side of the beaker; these apparently different deposits had, however, practically the same decomposition points, and their mechanical separation led to no result. In nearly all cases the more sparingly soluble portions had the higher decomposition points (up to 170°), and seemed to be the more impure.

It was also observed that specimens decomposing at about 140°, when left exposed to the air at the ordinary temperature, sometimes underwent some change, and then did not decompose until 160—165°; this behaviour was not due to loss of solvent, and is referred to later.

Up to this time the use of aqueous solvents for the purification of the diol had been avoided because it had been observed that hot aqueous alcohol and acetic acid decomposed the compound; as a last resource, however, aqueous acetone was tried, with the following results.

When any of the preparations of impure diphenylsilicanediol, which decomposes above about 135°, was dissolved in acetone, and the solution diluted with a small proportion of water, the liquid became milky, and when left to evaporate at the ordinary temperature the milky fluid deposited colourless prisms. After a few days' time practically the whole of the diol had crystallised out, and was easily separated from the milky mother liquors, which passed unchanged through an ordinary filter; as a rule, in fact, the crystals were so large that the mother liquor might be merely decanted from them.

The milkiness of the original solutions appeared to be a rough measure of the impurity in the diol; according to this criterion, the preparations obtained by precipitating the alkaline solution with ammonium chloride were the least impure, whilst those obtained by decomposing the dichloride with water were less impure than those produced by precipitating the diol with hydrochloric acid. The crystals which separated from the milky fluid were covered with an oily film, which was easily removed by washing them with cold chloroform. When the washed crystals were again dissolved in acetone, and the solution was diluted with a little water, a milky fluid was again produced, but for any given sample the milkiness was far less pronounced than it was at the first treatment. The crystals which were subsequently deposited, when again washed with chloroform and then dissolved in acetone, usually gave solutions which did not become milky on the addition of water, but which immediately deposited a crystalline precipitate if sufficiently diluted. In those cases in which a milkiness was produced, the purification was still incomplete, but after a repetition of the operations a pure compound was obtained.

The crystalline substance, isolated in this way and then finally recrystallised from hot ethyl acetate or acetone, was pure diphenylsilicanediol; the milky mother liquors, which often remained unchanged in appearance during many months, and the chloroform washings of the crystals, contained the relatively small quantity of impurity, which apparently could not be removed by recrystallisation from anhydrous solvents, and seemed so greatly to affect the decomposition point of the pure diol. This impurity, so far as has been ascertained, is usually a mixture of three or four compounds.

By the use of aqueous acetone and chloroform alternately, it was also possible to isolate diphenylsilicanediol from the recrystallised preparations decomposing at about 115°, which had been originally obtained by precipitation with acetic acid. Such preparations gave with aqueous acetone, solutions which, as a rule, were not very milky, but from which on spontaneous evaporation, there gradually separated both crystals and oil; the latter was easily removed with the aid of cold chloroform, and the crystalline residue was redissolved in aqueous acetone. The solutions then gave a deposit containing far less oil, and by a repetition of these processes the pure diol was finally obtained. When two or three air-dried preparations, which had been obtained from the potassium derivative by precipitation with acetic acid and then kept during some weeks, were examined in this way, they were found to be highly impure, and apparently the longer a sample had been kept the greater the proportion of impurity.

Diphenylsilicanediol, $SiPh_2(OH)_2$.

The various samples of diphenylsilicanediol, isolated from the different preparations by the method described, were carefully compared; they all had the characteristics of a pure compound, and were identical with one another:

0·1480 gave 0·3605 CO_2 and 0·0743 H_2O. C=66·4; H=5·6.
0·1480 „ 0·0412 SiO_2. Si=13·1.
$C_{12}H_{12}O_2Si$ requires C=66·6; H=5·6; Si=13·1 per cent.

Diphenylsilicanediol crystallises from ether, ethyl acetate, acetone, etc., in long, colourless needles or prisms, which often exceed 20 mm. in length; when its solutions in ethyl acetate evaporate spontaneously, it is sometimes obtained in large, well-defined crystals, suitable for goniometrical measurement.

It is practically insoluble in water or light petroleum, only sparingly soluble in cold chloroform, and very moderately so in boiling benzene, but it dissolves more readily in warm ether, and freely in boiling ethyl acetate or acetone.

All the freshly prepared, air-dried specimens of diphenylsilicanediol, purified in the manner described above, and finally recrystallised from ethyl acetate, showed at first the same behaviour when they were heated and directly compared; they began to sinter slightly at about 125°, and if then the temperature was slowly raised, they liquefied completely at about 128—132°, and a vigorous effervescence was observed owing to the escape of steam. In the case of any given sample, however, the temperature at which decomposition set in and complete liquefaction took place, varied slightly with the conditions of the experiment, principally with the rate of heating, but also with the state of division of the substance.

The temperatures just given, and most [illegible] decomposition points recorded in this paper, were observed when the rate of heating (about 100°) was a rise of about 10° per minute.

Although up to a certain time many freshly prepared samples of the pure diol had been heated, none had shown a decomposition point above 132°, and it seemed that the behaviour of the pure compound was invariable. When, however, four such preparations were examined again some two months after they had been obtained, one of them seemed to have undergone some change, and further observations were made.

One of these specimens, *A*, had been kept in a loosely-covered beaker, exposed to the laboratory air, and one of them, *B*, in a closed weighing-bottle; the other two, *C* and *D*, had been kept on clock glasses in a desiccator which contained a little damp soda-lime. The specimens *A* and *B* had not changed in appearance, and consisted of transparent needles. The specimen *C* seemed to have changed very slightly in appearance as the needles seemed somewhat opaque in parts. The specimen *D*, which consisted of rather small crystals, had obviously undergone some change, the previously transparent needles having become white and opaque; although this specimen sometimes decomposed completely below about 132°, it usually showed no signs of change until about 150°, and decomposed with effervescence at about 155—160°; further, it was no longer readily and completely soluble in a 5 per cent. aqueous solution of potassium hydroxide, but gave a very small proportion of a flocculent substance, which did not dissolve in the course of about ten minutes.

The other three specimens, *A*, *B*, and *C*, usually decomposed completely at 128—132°, but occasionally one of them did not sinter until about 150°, and decomposed with effervescence at about 155—159°; they were all completely soluble in a 5 per cent. aqueous solution of potassium hydroxide.

The results of a great many more experiments with the samples *A*, *B*, and *C*, and with various freshly prepared pure specimens, proved that diphenylsilicanediol might show one of two very different decomposition points; when six to eight melting-point tubes, all containing the same finely powdered sample, were heated simultaneously, the contents of one, or possibly two, of the tubes might not decompose until about 145° or even 158°, those of all the others having completely liquefied below 132°.

Now as it is most improbable that the observed difference in behaviour between identical samples under as nearly as possible identical conditions could be due merely to a difference in the rate of decomposition, it seems necessary to conclude that diphenylsilicanediol is dimorphous; that the crystalline form which is deposited from solvents and which decomposes below 132° may pass into a more stable one, which does not decompose until about 160°.

This conclusion, which appears to be fully established, affords an explanation of many of the apparently anomalous facts recorded in this paper. In the first place, it is obvious from the behaviour of the pure compound, that the change in crystalline form which sometimes occurs is due to some inappreciable and fortuitous difference in the experimental conditions; consequently, it is not only possible, but highly probable, that the presence of impurity of a particular kind might condition the change in crystalline form, especially if the impurity were isomorphous with the form which is stable at the higher temperature. The fact that all specimens of diphenylsilicanediol containing a certain proportion of those substances which are insoluble in potassium hydroxide solution have always, and those containing traces of such impurities have generally, the high decomposition point, would thus be explained; as these impurities are probably trianhydrotrisdiphenylsilicanediol and tetra-anhydrotetrakisdiphenylsilicanediol (compare following paper), neither of which would be melted at 132°, the presence of even a trace of either substance might cause the crystalline transformation of the diol to take place.

The fact that those impure specimens of the diol which contai small quantities of substances soluble in potassium hydroxi solution, and which decompose at about 118°, have a much higher decomposition point after they have been crystallised in presence of an acid, may also be accounted for; the impurity which lowers the decomposition point of the diol is some compound or mixture of low melting point which is changed by the acid into one of the above-named substances of high melting point; experimental evidence which strongly supports this assumption is given later (p. 2141).

The spontaneous rise in decomposition point which was often observed in the case of impure samples of the diol might, of course, have been apparent only, that is to say, the sample might not have changed until its decomposition point was being taken; in any case, unless the specimen were free from alkali and acid, a change in the decomposition point might well occur as the result of chemical changes in the impurity present, or in the diol itself; such changes might lead to the formation of the substance or substances which favour the crystalline transformation of the diol.

So far the only instance in which a highly purified sample appears to have changed is that of the specimen *D*, referred to above; whatever may be its cause or its nature, this change was only very superficial, and the opaque crystals immediately became transparent when they were moistened with acetone.

One further point remains to be considered, namely, how Martin was led to believe that the preparations which he regarded as isomeric diphenylsilicols could be transformed one into the other by the methods which he describes (*loc. cit.*). According to his statements, when the "isomeride" decomposing at about 160° was dissolved in an aqueous solution of potassium hydroxide, and the solution then treated with acids, the "isomeride" decomposing at about 144° was obtained, but if alcoholic potassium hydroxide was used, the original "isomeride" decomposing at about 160° was precipitated. These statements are doubtless incorrect in so far as any question of isomerism is concerned, but it is possible that the actual observations are to be accounted for as follows: The crude preparation decomposing at about 160° contained a considerable proportion of impurity which was insoluble in an aqueous solution of potassium hydroxide; when aqueous alkali was used and this impurity became visible, it was separated by filtration before the solution was acidified, so that the precipitated diol was less impure than the original sample, and decomposed at a rather lower temperature. When, however, the original sample was dissolved in alcoholic potassium hydroxide, the impurity was not precipitated, or was only partly precipitated, and consequently the diol finally obtained on the addition of an acid was just as impure as before, and decomposed at approximately the same temperature as the original sample.

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CCXXIV.—*Organic Derivatives of Silicon. Part XVII. Some Condensation Products of Diphenylsilicanediol.*

By Frederic Stanley Kipping.

One of the main factors that has retarded the development of the chemistry of silicon compounds is, undoubtedly, the insolubility in neutral solvents of all those inorganic derivatives which contain combined oxygen. This insolubility, of course, may be attributed, at any rate in part, to the great molecular complexity of all such compounds, which apparently is the result of a process of condensation brought about by the elimination of the elements of water from two or more molecules, such as those of silicic acid, containing the group $>Si\cdot OH$.

Now when the silicon atom in such a group is directly combined with hydrocarbon radicles, the resulting compounds have properties very different from those of the inorganic silicates; although the tendency to undergo condensation is still very marked, even in substances such as the alkyl and aryl derivatives of the type $R_3Si\cdot OH$ (Kipping, Trans., 1907, **91**, 718), the condensation products of such organic derivatives are still soluble in many neutral solvents, and, consequently, lend themselves to the ordinary methods of investigation.

It would seem, therefore, that our knowledge of the chemistry of silicon is more likely to be extended by a study of the organic derivatives of this element than by that of its mineral compounds.

Now during the investigation of the products of hydrolysis of dichlorodiphenylsilicane (this vol., p. 2108) it was found that diphenylsilicanediol was very easily decomposed by acids and by alkalis, and, even when particular precautions were taken in working with this compound, it was difficult to avoid the formation of oily or glue-like substances.

In view of the probability that these various by-products were mixtures of compounds formed by the condensation of diphenylsilicanediol, and of the possibility that the study might throw some light on the nature of the complex mineral silicates, it seemed worth while to attempt the otherwise uninviting task of isolating the different components of the oils or glues in question; the results of this work are described in the present paper.

So far, four compounds, which are directly related to one another and to diphenylsilicanediol, have been obtained in a pure state from these mixtures, but from observations made during this investigation and from the results of some experiments carried out by Martin (compare *Ber.*, 1912, **45**, 1139, and footnote, this vol., p. 2108), it would appear that several other condensation products, more complex than those described below, may be obtained without difficulty.

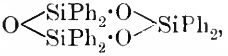
As was anticipated, all these four compounds are derived from diphenylsilicanediol by the loss of the elements of water; subsequent experiments with pure diphenylsilicanediol have shown that their formation is due to the action of traces of alkali or of small quantities of acids on this diol.

The simplest of these condensation products is a compound of the constitution $HO\cdot SiPh_2\cdot O\cdot SiPh_2\cdot OH$, which is formed from two molecules of diphenylsilicanediol by the loss of one molecule of water, and which is called *anhydrobisdiphenylsilicanediol*, in accordance with the scheme of nomenclature already suggested (this vol., p. 2107).

The second condensation product of diphenylsilicanediol, which has been isolated, is produced from three molecules of diphenylsilicanediol by the loss of two molecules of water; this compound has the constitution $HO\cdot SiPh_2\cdot O\cdot SiPh_2\cdot O\cdot SiPh_2\cdot OH$, and, therefore, is named *dianhydrotrisdiphenylsilicanediol.*

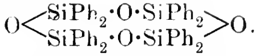
Anhydrobisdiphenylsilicanediol and dianhydrotrisdiphenylsilicanediol are both beautifully crystalline compounds, which are freely soluble in most of the ordinary solvents; the former is rapidly converted into a soluble potassium derivative when it is treated with a cold dilute solution of potassium hydroxide, but the latter is not appreciably changed by this reagent.

The other two condensation products of the diol which have been obtained are "multimolecular diphenylsilicones"; the one melts at 188—189°, and is doubtless a *trianhydrotrisdiphenylsilicanediol* of the constitution



$$O\left<\begin{matrix}SiPh_2\cdot O\\ SiPh_2\cdot O\end{matrix}\right>SiPh_2,$$

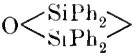
whilst the other melts at 200—201°, and must be regarded as a *tetra-anhydrotetrakisdiphenylsilicanediol* of the constitution



$$O\left<\begin{matrix}SiPh_2\cdot O\cdot SiPh_2\\ SiPh_2\cdot O\cdot SiPh_2\end{matrix}\right>O.$$

Trianhydrotrisdiphenylsilicanediol is easily obtained by heating diphenylsilicanediol, or by treating it with acetic chloride; tetra-anhydrotetrakisdiphenylsilicanediol is formed, together with the tri-anhydro-compound, when anhydrobisdiphenylsilicanediol is treated with acetyl chloride, and also when dichlorodiphenylsilicane is hydrolysed with less than the theoretical quantity of an aqueous solution of an alkali hydroxide.

From the observations so far made it would seem that all the above compounds are produced from diphenylsilicanediol by a process of condensation, and that the "multimolecular silicones" are not directly formed by the polymerisation of diphenylsilicone. It is, in fact, rather doubtful whether diphenylsilicone is produced or not by the elimination of water from the diol; oily products, which possibly contain this silicone, are very easily formed from diphenylsilicanediol under various conditions, but as such oils are complex mixtures, it has not yet been found possible to identify all their components. The evidence pointing to the presence in them of diphenylsilicone is, that when the oils have been freed so far as possible from diphenylsilicanediol, anhydrobisdiphenylsilicanediol, and dianhydrotrisdiphenylsilicanediol, they yield trianhydrotrisdiphenylsilicanediol and tetra-anhydrotetrakisdiphenylsilicanediol on treatment with hydrochloric acid in alcoholic solution; this evidence, however, is inconclusive.

The existence of a dianhydrobisdiphenylsilicanediol of the constitution  $\mathrm{O}<\begin{matrix}\mathrm{SiPh_2}\\\mathrm{SiPh_2}\end{matrix}>\mathrm{O}$, derived from one molecule of anhydrobisdiphenylsilicanediol by the loss of one molecule of water, is also doubtful; the facts that anhydrobisdiphenylsilicanediol is relatively very stable towards heat, and that, when treated with acetyl chloride, it gives tetra-anhydrotetrakisdiphenylsilicanediol (mixed with trianhydrotrisdiphenylsilicanediol), seem to show that the closed chain of two silicon and two oxygen atoms is not easily formed.

A "termolecular diphenylsilicone," melting at 188°, to which he gave the constitution assigned above to trianhydrotrisdiphenylsilicanediol, has been previously described by Dilthey (*Ber.*, 1905, **38**, 4132), and was also obtained by Martin (*loc. cit.*); judging by its melting point, the author's trianhydrotrisdiphenylsilicanediol is identical with Dilthey's crystalline "termolecular silicone," but there are certain statements in Dilthey's paper which are rather in conflict with this view.

By heating diphenylsilicanediol, Dilthey obtained a gelatinous mass, to which, from the results of analyses and molecular-weight determinations, he assigned the formula $[\mathrm{SiPh_2O}]_3$; this gelatin, according to his statements, was converted into the crystalline "termolecular silicone" when it was brought into contact with a drop of alcohol or acetic anhydride, a change which Dilthey regarded as a process of polymerisation.

The molecular weight of this crystalline silicone was found to be 605 in benzene solution, and apparently, from the statement, "rasches Erhitzen ist erförderlich," its melting point varied with the rate of heating; it was partly converted into the gelatin when it was recrystallised from benzene.

Now the author's trianhydrotrisdiphenylsilicanediol gave a molecular weight of 490 in benzene solution, its melting point did not vary with the rate of heating, and it was not changed in any way by benzene or other neutral solvents. In view of these facts the identity of trianhydrotrisdiphenylsilicanediol and Dilthey's "termolecular silicone" might be questioned, but in the author's opinion there is no sufficient reason to do so; the variability of the melting point of Dilthey's preparation, if, in fact, such variability was observed, and the supposed partial transformation of this crystalline compound into a gelatinous substance, would be accounted for if the samples had not been completely separated from the other products which are formed by the action of heat on diphenylsilicanediol.

With regard to the gelatinous mass, which Dilthey considered to be convertible into the crystalline silicone, the author's experiments seem to show conclusively that it was merely a mixture of trianhydrotrisdiphenylsilicanediol and other dehydration or condensation products of diphenylsilicanediol (compare p. 2137).

Martin (*loc. cit.*) states that his observations confirmed those of Dilthey as regards the existence of two forms of a "termolecular diphenylsilicone," but he does not give any particulars in support of this statement, except that various viscid masses, obtained by treating the diol with hydrochloric acid, gave the crystalline "termolecular silicone" when they were warmed with acetic anhydride; here, again, as in the case of Dilthey's gelatin, the crystalline compound was probably already present in the viscid mass, or was produced from some unchanged diphenylsilicanediol by the action of the acetic anhydride, and the experiments do not afford the slightest evidence of the existence of a gelatinous "termolecular diphenylsilicone."

In Martin's paper there is also some account of a substance melting at 100—111°, of which, however, no analysis is given, and a reference to two other crystalline compounds, melting at 125° and 186° respectively, which were obtained in very small quantities. The first of these substances (m. p. 100—111°) was probably an impure preparation of anhydrobisdiphenylsilicanediol, which melts at 113—114°; whereas the third was possibly a mixture of trianhydrotrisdiphenylsilicanediol and tetra-anhydrotetrakisdiphenylsilicanediol (compare p. 2140); no compound melting at 125° has been obtained during the present investigation.

EXPERIMENTAL.

When dichlorodiphenylsilicane is hydrolysed with cold water, a considerable proportion of the product consists of a pale yellow oil, which is readily soluble in cold chloroform (this vol., p. 2114), and also in cold alcohol; an oil having these properties is also obtained as the only product when the dichloride is decomposed with a cold concentrated solution of ammonium hydroxide (this vol., p. 2115).

Similar oils are, or may be, obtained, owing doubtless to the action of acids, during the recrystallisation of the crude diphenylsilicanediol, prepared by some of the methods already described (pp. 2115, 2119). If, however, the crude diphenylsilicanediol contains traces of potassium hydroxide, as probably do those samples obtained by neutralising solutions of its potassium derivative with acetic acid (p. 2116), the original by-products, or those formed during recrystallisation, are of a different character; they are more glue-like in consistency, and although readily soluble in chloroform are only partly soluble in cold ethyl alcohol.

All those oily by-products which are soluble in ethyl alcohol seem to be mixtures of anhydrobisdiphenylsilicanediol (m. p. 113—114°) and dianhydrotrisdiphenylsilicanediol (m. p. 111—112°), containing also a small proportion of trianhydrotrisdiphenylsilicanediol (termolecular diphenylsilicone) and a variable but very considerable proportion of other components; the three crystalline compounds just named may be isolated in the following manner: The oil is dissolved in a considerable quantity of chloroform, and the solution is diluted with light petroleum until it begins to turn turbid. If, when the solution is allowed to evaporate at the ordinary temperature, it gives a crystalline deposit, it is left undisturbed until an oil begins to separate with the crystals; the mother liquor is then decanted. If, however, the solution merely deposits an oil, a considerable quantity of light petroleum is added in order to precipitate a suitable proportion of the dissolved substance, and the clear solution is then decanted. The crystalline deposit or the precipitated oil is again dissolved in chloroform, and the solution, having been mixed with light petroleum, is left to evaporate at the ordinary temperature; the original mother liquors are either left to evaporate spontaneously, or a further proportion of the dissolved matter is immediately precipitated with the aid of light petroleum.

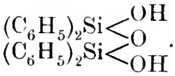
As the result of such operations, carried out systematically, the original oil is separated into various fractions, some of which give crystalline deposits when their solutions in a mixture of chloroform and light petroleum are evaporated at the ordinary temperature.

These crystalline fractions sometimes contain a very small quantity of diphenylsilicanediol, which is now easily and almost completely removed by treatment with cold chloroform, in which the diol is only sparingly soluble. The chloroform solution is then evaporated, the residue is dissolved in a very little ether (or ethyl acetate), and the solution is diluted with light petroleum until a turbidity is produced. The crystalline material which first separates from such solutions at the ordinary temperature generally contains, or consists principally of, trianhydrotrisdiphenylsilicanediol; as this compound is rather sparingly soluble in ether (or ethyl acetate) and practically insoluble in light petroleum, its separation from the other two components of the mixture is accomplished by further systematic treatment with these solvents.

The trianhydrotrisdiphenylsilicanediol having been removed as completely as possible, the ethereal-petroleum solution is evaporated, the residue is again dissolved in a mixture of chloroform and light petroleum, and the solution is left to evaporate at the ordinary temperature. The first crystalline deposit which is then obtained may consist almost entirely of anhydrobisdiphenylsilicanediol; the subsequent fractions, however, are equilibrium mixtures of this substance and dianhydrotrisdiphenylsilicanediol. The separation of the two compounds just named from one another is a matter of great difficulty; as fractional crystallisation gives very unsatisfactory results, the most convenient method to adopt is a mechanical one. The chloroform-petroleum solution is evaporated slowly at the ordinary temperature in order to obtain large crystals; the dianhydrotrisdiphenylsilicanediol is then deposited in massive, transparent, rhomboidal crystals, which are distinguishable by inspection from the prisms of anhydrobisdiphenylsilicanediol. The crystals of the former having been picked out, the residue is crystallised again under the same conditions as before, and any crystals of the dianhydrotrisdiphenylsilicanediol are removed from the deposit; these operations are continued until the separation is as complete as possible, and the two products are then further purified by recrystallisation from chloroform containing a little light petroleum.

When the original oily by-product has been repeatedly and systematically fractionated with the aid of chloroform and light petroleum in the manner described, and the various crystalline mixtures of anhydrobisdiphenylsilicanediol, dianhydrotrisdiphenylsilicanediol, and trianhydrotrisdiphenylsilicanediol have been removed, there remains a considerable proportion of the original material as a viscid oil, from which no further crystalline deposit can be obtained. This oil is no longer completely soluble in cold alcohol; a large proportion of it dissolves freely, leaving a viscid, glue-like mass. These products are referred to later (p. 2141).

Anhydrobisdiphenylsilicanediol,



$$\begin{array}{l}(C_6H_5)_2Si<^{OH}_{O}\\(C_6H_5)_2Si<_{OH}\end{array}.$$

The mechanical separation of this compound from dianhydrotrisdiphenylsilicanediol having been carried out as far as possible, the crude substance is recrystallised from a mixture of chloroform and light petroleum at the ordinary temperature; it is thus obtained in beautiful, transparent crystals, melting sharply at 113—114°.

Anhydrobisdiphenylsilicanediol was thus isolated from the by-products previously mentioned, and its occurrence in these oils shows that it is produced from diphenylsilicanediol by the action of hydrochloric acid, and also by the action of a concentrated solution of ammonium hydroxide on dichlorodiphenylsilicane.

Two different preparations were analysed:

0·1726 gave 0·4396 CO_2 and 0·0850 H_2O. C = 69·5; H = 5·5.
0·1376 „ 0·3504 CO_2 „ 0·0700 H_2O. C = 69·5; H = 5·6.
$C_{24}H_{22}O_3Si_2$ requires C = 69·7; H = 5·3 per cent.

Molecular-weight determinations were made by the cryoscopic method in benzene solution:

0·53 in 11·2 benzene gave $\Delta t = -0·4$. M.W. = 579.
0·234 „ 11·3 „ „ $\Delta t = -0·16$. M.W. = 539.
0·617 „ 13·3 „ „ $\Delta t = -0·375$. M.W. = 601.
$C_{24}H_{22}O_3Si_2$ requires M.W. = 414.

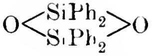
These results do not agree well with the theoretical values, probably because the hydroxy-compound is associated in benzene solution; other determinations in acetic acid or alcoholic solution were not made, as the compound is changed by these solvents. There is, however, a certain amount of independent evidence in favour of the molecular formula given above, as will be explained later.

Anhydrobisdiphenylsilicanediol crystallises well from benzene or from a mixture of benzene and light petroleum in transparent prisms, but from ether, ethyl acetate, and acetone it is often deposited as an oil; it also separates from aqueous acetone as an oil, which does not crystallise readily. It is very soluble in all the anhydrous solvents named above, except cold light petroleum, in which it is practically insoluble.

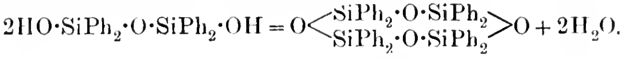
Anhydrobisdiphenylsilicanediol is converted into a soluble potassium derivative when it is treated with a cold solution of potassium hydroxide; small crystals, when placed on the surface of such a solution, often rotate, or move about rapidly, as they dissolve. With acetic acid the solution gives a crystalline precipitate, which is sparingly soluble in cold chloroform, and which is doubtless diphenylsilicanediol.

Anhydrobisdiphenylsilicanediol is very readily soluble in cold methyl or ethyl alcohol; when such solutions are evaporated at the ordinary temperature, it separates to a very great extent unchanged. It is, however, partly decomposed by these solvents, and when the solutions are kept for a long time, or heated, they deposit a white powder, which seems to be a mixture of condensation products. This transformation takes place so slowly that it is very incomplete, even after the solutions have been boiled during about an hour.

Anhydrobisdiphenylsilicanediol is stable at 100°, and even at 200° it seems to be only slowly decomposed, bubbles of aqueous vapour escaping from the liquid mass; when heated more strongly in a test-tube over a flame, a rapid effervescence takes place, a very pronounced odour of burnt petroleum is observed, and after a short time decomposition is practically complete. The residue, which solidifies on being cooled, is not completely soluble in warm ethyl acetate; the insoluble matter is a white powder, which is probably a highly complex condensation product. The soluble portion separates from the filtered solution in well-defined crystals; when these are heated at 110° about one-half of them become opaque, whilst the rest remain transparent; the former melt at about 184°, and consist principally of tetra-anhydrotetrakisdiphenylsilicanediol (m. p. 200—201°), whilst the latter melt at about 188° and consist of practically pure trianhydrotrisdiphenylsilicanediol (compare p. 2140).

Since it would seem that under the above conditions a dianhydrobisdiphenylsilicanediol of the constitution  $O{<}\begin{matrix}SiPh_2\\SiPh_2\end{matrix}{>}O$ is not produced, it may be inferred that a closed chain of two silicon and two oxygen atoms is not formed so readily as one containing three silicon and three oxygen atoms, or four silicon and four oxygen atoms. The production of trianhydrotrisdiphenylsilicanediol is not easily accounted for, except on the assumption that at the high temperature employed some of the anhydrobisdiphenylsilicanediol is hydrolysed by the water which is formed during the operation. Whether this is so or not, the formation of the trianhydro-compound seems to show that the closed chain of six atoms is more stable than that of eight. It is also of interest to note that the behaviour of anhydrobisdiphenylsilicanediol at high temperatures differs from that of anhydrobisdibenzylsilicanediol (p. 2151), inasmuch as the latter, apparently, does not give a product corresponding with tetra-anhydrotetrakisdiphenylsilicanediol.

Anhydrobisdiphenylsilicanediol dissolves freely in acetyl chloride at the ordinary temperature, and when the solution is evaporated in a desiccator over soda-lime it gives a crystalline deposit, which consists essentially, if not entirely, of tetra-anhydrotetrakisdiphenylsilicanediol. The presence of trianhydrotrisdiphenylsilicanediol was not detected in this product, and although a relatively small quantity of a powder sparingly soluble in ethyl acetate was formed, and the purification of the tetra-anhydrotetrakisdiphenylsilicanediol was thereby rendered somewhat troublesome, the main reaction was obviously expressed by the equation:



$$2HO\cdot SiPh_2\cdot O\cdot SiPh_2\cdot OH = O{<}\begin{matrix}SiPh_2\cdot O\cdot SiPh_2\\ SiPh_2\cdot O\cdot SiPh_2\end{matrix}{>}O + 2H_2O.$$

Dianhydrotrisdiphenylsilicanediol, $HO\cdot SiPh_2\cdot O\cdot SiPh_2\cdot O\cdot SiPh_2\cdot OH$.

The large crystals of this compound, which have been separated from the anhydrobisdiphenylsilicanediol mechanically (p. 2131), are practically free from impurity, and are merely recrystallised from a mixture of chloroform and light petroleum; the pure substance is then deposited in beautiful, rhomboidal prisms, melting sharply at 111—112°.

It was thus obtained from the same by-products as those which gave anhydrobisdiphenylsilicanediol; it is therefore formed by the action of acids on diphenylsilicanediol, and by the action of a concentrated solution of ammonium hydroxide on dichlorodiphenylsilicane.

Two different samples were analysed:

0·1941 gave 0·5010 CO_2 and 0·0937 H_2O. C = 70·4; H = 5·3.
0·1826 „ 0·4726 CO_2 „ 0·0893 H_2O. C = 70·6; H = 5·4.
$C_{36}H_{32}O_4Si_3$ requires C = 70·4; H = 5·2 per cent.

Its molecular weight was determined by the cryoscopic method in benzene solution:

0·283 in 13·3 benzene gave $\Delta t = -0·14$. M.W. = 745.
0·617 „ 13·3 „ „ $\Delta t = -0·32$. M.W. = 766.

One determination, possibly not a very trustworthy one, was made in chloroform by the ebullioscopic method:

0·48 in 18·5 chloroform gave E = 0·13. M.W. = 730.

As the calculated molecular weight for a compound of the composition $C_{36}H_{32}O_4Si_3$ is 613, the above experimental values, like those obtained in the case of anhydrobisdiphenylsilicanediol, are very much too high, and indicate the presence of associated molecules in the given solvents. If, however, the average results obtained with the two compounds in benzene solution are compared, it will be seen that the difference in molecular weight is found by experiment to be about 182, which corresponds closely with the calculated difference. Further evidence in support of the formula assigned to dianhydrotrisdiphenylsilicanediol is afforded by the fact that this compound may be readily and quantitatively converted into the "termolecular silicone" (trianhydrotrisdiphenylsilicanediol) as shown later.

Dianhydrotrisdiphenylsilicanediol resembles anhydrobisdiphenylsilicanediol in its general behaviour towards solvents; it is very readily soluble in chloroform, ether, acetone, or ethyl acetate, but practically insoluble in cold light petroleum. It also dissolves freely in cold benzene, from which it separates in massive, transparent, rhomboidal crystals; these contain benzene, which they slowly lose on exposure to the air:

1·0942 lost 0·1244 at 100°. $C_6H_6 = 11·4$.

$C_{36}H_{32}O_4Si_3,C_6H_6$ requires $C_6H_6 = 11·3$ per cent.

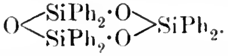
From aqueous acetone dianhydrotrisdiphenylsilicanediol separates as an oil which does not crystallise readily; it dissolves freely in cold methyl alcohol, but, like anhydrobisdiphenylsilicanediol, it is slowly acted on by this solvent, and the solution deposits a colourless powder, a part of which is insoluble in ethyl acetate and doubtless consists of some condensation product of very high molecular weight.

Dianhydrotrisdiphenylsilicanediol is not appreciably acted on by a 5 per cent. aqueous solution of potassium hydroxide; small crystals left in contact with such a solution show no visible diminution in size, even after many hours. This marked difference in behaviour between anhydrobis- and dianhydrotris-diphenylsilicanediol is very useful for distinguishing the two compounds and for testing the purity of the former. Alcoholic potassium hydroxide hydrolyses dianhydrotrisdiphenylsilicanediol at the ordinary temperature, giving a solution from which acetic acid precipitates a colourless compound; this precipitate is only very sparingly soluble in cold chloroform, and doubtless consists of diphenylsilicanediol.

Dianhydrotrisdiphenylsilicanediol seems to be decomposed by heat rather more readily than is anhydrobisdiphenylsilicanediol, and at about 170° it begins to lose water with appreciable rapidity. When it is heated over a free flame the escaping steam causes an effervescence, and a strong odour of burnt petroleum is noticed; the residue solidifies readily, and when crystallised from ethyl acetate gives pure trianhydrotrisdiphenylsilicanediol, which, apparently, is the principal, if not the only, product of the reaction.

Dianhydrotrisdiphenylsilicanediol is readily soluble in acetyl chloride; when the solution is slowly evaporated in a desiccator over soda-lime, trianhydrotrisdiphenylsilicanediol is deposited in well-defined crystals, and the yield seems to be quantitative. The readiness with which the dianhydro- is converted into the trianhydro-compound may be taken as confirmatory evidence of the supposed relation between the two compounds; also as indicative of the stability of the closed chain containing three silicon and three oxygen atoms.

Trianhydrotrisdiphenylsilicanediol,



$$O\left<\begin{matrix}SiPh_2\cdot O\\ SiPh_2\cdot O\end{matrix}\right>SiPh_2.$$

This compound is present in relatively small quantities in the oil which is formed when dichlorodiphenylsilicane is decomposed with a concentrated solution of ammonium hydroxide, and also in the oil which is formed when diphenylsilicanediol is heated with solvents in presence of traces of acids; it is also present, usually in larger quantities, in those glue-like products which are formed by the action of traces of alkalis on the diol. One method for the isolation of this compound from such mixtures has already been described (p. 2130), but a much simpler process may sometimes be used at the sacrifice of any anhydrobisdiphenylsilicanediol and dianhydrotrisdiphenylsilicanediol which are contained in the mixture; the oily product is extracted with an aqueous solution of potassium hydroxide, the washed residue is treated with cold methyl alcohol, and the undissolved crystalline matter is recrystallised from ethyl acetate. In this way pure trianhydrotrisdiphenylsilicanediol is sometimes obtained very easily; in many cases, however, the crystals which are deposited from the ethyl acetate solution are a mixture of trianhydrotrisdiphenylsilicanediol and tetra-anhydrotetrakisdiphenylsilicanediol, the separation of which is rather troublesome (p. 2142).

As stated above, trianhydrotrisdiphenylsilicanediol is easily obtained from dianhydrotrisdiphenylsilicanediol, and is also formed together with tetra-anhydrotetrakisdiphenylsilicanediol by the action of heat on anhydrobisdiphenylsilicanediol; it is most conveniently prepared by heating pure diphenylsilicanediol first at about 150° and finally at about 180° until approximately the theoretical loss in weight has taken place.

As soon as the temperature of the bath rises to about 140°, the diol rapidly liquefies, and a vigorous effervescence is observed; after about ten minutes at this temperature, the effervescence practically ceases, but the decomposition is still incomplete, and the loss in weight is only about 6 per cent. (starting with about 0·5 gram of the diol). The temperature is then slowly raised to about 180° in the course of about twenty-five minutes, at the end of which time the loss in weight is about 8·0 per cent., which corresponds approximately with the theoretical quantity (8·3 per cent.). The cooled residue may crystallise, or it may remain for a long time as a transparent glass; if, however, the latter is again heated at about 120—130° for a moment, or rubbed with a glass rod, or treated with small quantities of various solvents, it gives a crystalline mass of trianhydrotrisdiphenylsilicanediol, which is purified by recrystallisation from ethyl acetate.

Although the pure diol may have been heated until approximately the theoretical loss in weight has occurred, the product does not consist of pure trianhydrotrisdiphenylsilicanediol, and the ethyl acetate mother liquors contain an appreciable proportion of an oily substance, which is readily soluble in light petroleum containing a little ethyl acetate; the nature of this oil has not been determined, but it seems possible that it may contain diphenylsilicone and anhydrobisdiphenylsilicanediol.

In view of the above results it seems improbable that the gelatin obtained by Dilthey by heating diphenylsilicanediol at 140° consisted of or contained any silicone isomeric with trianhydrotrisdiphenylsilicanediol (m. p. 188°); his product was probably a supercooled impure form of the last-named compound.

Some quantitative experiments on the effect of heat on diphenylsilicanediol were made by Martin (*loc. cit.*), who found that at 140° there was a loss in weight of 13·3 per cent. at the end of five hours. In the above experiments the diol was heated in a test-tube, and the weight became practically constant in the time stated; as, however, the conditions were so different in the two sets of observations, the results are hardly comparable. A possible explanation of the high loss observed by Martin is, that atmospheric oxidation occurred, with subsequent loss of the oxidation product; this would account for the high percentage of silicon which Martin found in the residue.

Trianhydrotrisdiphenylsilicanediol may also be obtained by dissolving diphenylsilicanediol in excess of acetyl chloride, and evaporating the solution in a desiccator over soda-lime; although the residue consists mainly of trianhydrotrisdiphenylsilicanediol, it also contains a small proportion of tetra-anhydrotetrakisdiphenylsilicanediol, and, for the isolation of the former, repeated recrystallisation from ethyl acetate or acetone is necessary.

Trianhydrotrisdiphenylsilicanediol crystallises very well from cold ethyl acetate, and is very readily soluble in chloroform or benzene, sparingly so in cold ether, and practically insoluble in light petroleum and the two common alcohols. Its partial conversion into a gelatin, as described by Dilthey, by recrystallisation from chloroform, ether, or benzene, has never been observed; imperfectly purified samples give, it is true, deposits which are contaminated with a very viscid substance, but the pure compound gives only clean, lustrous crystals, and Dilthey's observations to the contrary are certainly incorrect, if his crystalline "termolecular silicone" is identical with trianhydrotrisdiphenylsilicanediol.

The pure compound melts very sharply at 188—189°, and its melting point does not vary with the rate of heating; Dilthey's statement that "rasches Erhitzen ist erförderlich" seems an indication that his specimen was not pure.

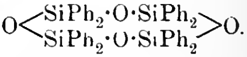
In view of these discrepancies between Dilthey's and the author's observations and of Martin's statement that his experiments confirmed those of Dilthey an analysis of the compound melting at 188—189° was made:

0·1560 gave 0·4154 CO_2 and 0·7600 H_2O. C = 72·6; H = 5·4.
$C_{36}H_{30}O_3Si_3$ requires C = 72·6; H = 5·0 per cent.

Its molecular weight was also determined by the cryoscopic method in benzene solution:

0·165 in 13·3 benzene gave $\Delta t = -0·114$. M.W. = 490.
0·302 ,, 13·3 ,, ,, $\Delta t = -0·214$. M.W. = 490.
0·383 ,, 13·3 ,, ,, $\Delta t = -0·29$. M.W. = 490.
0·427 ,, 16·4 ,, ,, $\Delta t = -0·272$. M.W. = 477.
$C_{36}H_{30}O_3Si_3$ requires M.W. = 594.

These results, which agree exceptionally well among themselves, are very different from those (609 and 601) obtained by Dilthey; they are, moreover, very considerably lower than the calculated value. As the readings were very constant and the author has no reason to doubt their accuracy, the fact that the observed are about 20 per cent. lower than the theoretical value cannot be accounted for; it will be seen, however, that corresponding results are obtained in the case of the similar but more complex compound described below.

Tetra-anhydrotetrakisdiphenylsilicanediol, 

$$O{<}\begin{matrix}SiPh_2\cdot O\cdot SiPh_2\\ SiPh_2\cdot O\cdot SiPh_2\end{matrix}{>}O.$$

This compound may be prepared, as stated above, by treating anhydrobisdiphenylsilicanediol with acetyl chloride; it is also formed, together with trianhydrotrisdiphenylsilicanediol, when anhydrobisdiphenylsilicanediol is heated alone, and, further, when those oily by-products which contain anhydrobisdiphenylsilicanediol (and other substances) are heated with an alcoholic solution of hydrochloric acid.

It may be obtained in one operation by gradually adding dichlorodiphenylsilicane to an aqueous solution of potassium hydroxide, but the most suitable conditions for its formation in this way have not been determined. When excess of potassium hydroxide is used, a clear solution of the potassium derivative of diphenylsilicanediol is formed (this vol., p. 2116); when, however, such a quantity of potassium hydroxide is present that the solution becomes acid to litmus after about two-thirds of the dichloro-compound have been added, the addition of the remainder results in the separation of a pasty solid. This product, having been washed with water and dried in the air, crystallises from ethyl acetate, but the solution deposits two kinds of crystals, which may be separated from one another mechanically. The larger proportion of the deposit consists of long, slender, not very well defined prisms, which melt at about 197°; the remainder consists of short, compact, well-defined crystals, which melt at about 184°, and which are referred to below.

The product, melting at about 197°, is slightly impure tetra-anhydrotetrakisdiphenylsilicanediol; when recrystallised several times from ethyl acetate its melting point becomes constant at 200—201°:

0·1362 gave 0·3636 CO_2 and 0·0606 H_2O. C=72·8; H=4·94.
0·1524 ,, 0·0472 SiO_2. Si=14·6.
$C_{48}H_{40}O_4Si_4$ requires C=72·6; H=5·0; Si=14·4 per cent.

Its molecular weight was determined by the cryoscopic method in benzene solution:

0·271 in 13·2 benzene gave $\Delta t = -0·15$. M.W.=685.
0·29 ,, 13·3 ,, ,, $\Delta t = -0·16$. M.W.=674.
0·546 ,, 13·3 ,, ,, $\Delta t = -0·30$. M.W.=669.
$C_{48}H_{40}O_4Si_4$ requires M.W.=792.

These results, like those obtained in the case of trianhydrotrisdiphenylsilicanediol, are about 20 per cent. lower than the calculated value, but as the readings were very sharp and constant, there is no reason to doubt their accuracy. In so far as the relation between tetra-anhydrotetrakisdiphenylsilicanediol and trianhydrotrisdiphenylsilicanediol is concerned, the determinations show a difference of about 189 as against a theoretical difference of 198; on the whole, therefore, the results support the molecular formulæ respectively assigned to these two compounds.

Tetra-anhydrotetrakisdiphenylsilicanediol is readily soluble in cold chloroform or benzene, only very moderately so in cold acetone or ethyl acetate, and very sparingly so in the common alcohols or light petroleum. It nearly always separates from warm ethyl acetate or acetone in long, slender, very imperfect prisms, but when crystallisation occurs at the ordinary temperature the compound is generally deposited in well-defined, almost rectangular plates, or in long, well-defined prisms. The crystals obtained from cold ethyl acetate solution become opaque at temperatures below 100°, but do not contain solvent.

The crystalline product melting at about 184° which was obtained together with tetra-anhydrotetrakisdiphenylsilicanediol in the manner described above, and separated from it mechanically, seemed to be a pure compound; when recrystallised from ethyl acetate at the ordinary temperature it gave massive, transparent, well-defined, rhomboidal crystals, melting fairly sharply at 184—186°, and sometimes of such a size that individual crystals weighed more than 0·5 gram. It also crystallised well from hot ethyl acetate and from cold acetone, giving transparent, almost rectangular plates, indistinguishable by inspection from those of tetra-anhydrotetrakisdiphenylsilicanediol, but which melted at 184—186°, instead of at 200—201°, which is the melting point of the last-named compound.

It was ultimately discovered that this apparently pure and beautifully crystalline compound, melting at 184—186°, was, in fact, a mixture of tetra-anhydrotetrakisdiphenylsilicanediol and trianhydrotrisdiphenylsilicanediol; by repeated fractional crystallisation, first from warm acetone, and then from ethyl acetate, it was gradually resolved into the pure compound, melting at 200—201°, and a small quantity of trianhydrotrisdiphenylsilicanediol.

It is obvious, therefore, that when tetra-anhydrotetrakisdiphenylsilicanediol separates from an ethyl acetate solution which contains a sufficient quantity of trianhydrotrisdiphenylsilicanediol, the two substances crystallise together, apparently in fixed proportions, giving a product of almost constant melting point. Moreover, massive, well-defined crystals of this product are far more easily obtained than are large crystals of pure tetra-anhydrotetrakisdiphenylsilicanediol; whereas the latter generally separates from warm ethyl acetate and acetone in slender prisms, quite unsuitable for goniometrical examination, the mixture melting at about 184—186°, is usually deposited in the well-defined, rectangular plates from the warm solvents, and in the massive, rhomboidal prisms from cold ethyl acetate.

Mixtures of trianhydrotrisdiphenylsilicanediol and tetra-anhydrotetrakisdiphenylsilicanediol, as already stated, are obtained from diphenylsilicanediol in various ways, and such mixtures sometimes have a very indefinite melting point of about 160—170°; if they are recrystallised from ethyl acetate at the ordinary temperature, they give a crystalline deposit, which, from a cursory ocular inspection, seems to be homogeneous; when, however, such deposits are heated on the water-bath, some of the crystals become white and opaque, others remain perfectly transparent. The latter are the crystals of trianhydrotrisdiphenylsilicanediol, whilst the former are a mixture of this compound with tetra-anhydrotetrakisdiphenylsilicanediol, similar to that described above. The two kinds of crystals may be separated mechanically, and the opaque ones, when fractionally crystallised from hot acetone, ultimately give the compound melting at 200—201°, and small quantities of the compound melting at 188—189°.

Formation of Trianhydrotrisdiphenylsilicanediol and Tetra-anhydrotetrakisdiphenylsilicanediol from Oily Mixtures.

The very viscid oil, which is obtained by the evaporation of the petroleum–chloroform mother liquors, from which anhydrobisdiphenylsilicanediol, dianhydrotrisdiphenylsilicanediol, and trianhydrotrisdiphenylsilicanediol have been separated as far as possible (p. 2131), seems to be practically free from these compounds; when fractionally precipitated from chloroform, with the aid of light petroleum, it gives oily products, some of which are readily, others only sparingly, soluble in cold methyl alcohol, but although a partial separation of the components of the mixture may thus be accomplished, none of the fractions gives a crystalline deposit. So far the nature of these final fractions has not been determined, but it is possible to obtain from them a considerable proportion of crystalline products by suitable methods.

When the crude, non-crystallisable oil is treated with methyl alcohol, most of it passes into solution quite freely, whilst a small quantity of a sparingly soluble oil separates, and remains undissolved even after the addition of a large volume of the alcohol; if, now, a few drops of hydrochloric acid are added to the solution, most of the dissolved oil is rapidly precipitated, and after some time the separation of crystals commences. The methyl-alcoholic solution is then poured off and left to evaporate spontaneously; the residual, very viscid oil is warmed for a short time with methyl alcohol containing a few drops of hydrochloric acid, and the following day the solution is decanted. If these operations are repeated daily, the sparingly soluble oil becomes more and more viscous and diminishes in quantity, whilst the methyl-alcoholic extracts slowly deposit crystals.

This crystalline product can hardly be present in the original mixture, and is doubtless formed by the action of the methyl-alcoholic hydrochloric acid on some substance or substances contained in the oil. It is possible, although it does not seem very probable, that these substances are anhydrobisdiphenylsilicanediol and dianhydrotrisdiphenylsilicanediol; if this possibility be excluded, the origin of the crystalline product may be the yet unknown diphenylsilicone, $SiPh_2O$.

The crystalline product just referred to is a mixture of trianhydrotrisdiphenylsilicanediol and tetra-anhydrotetrakisdiphenylsilicanediol; when repeatedly crystallised from ethyl acetate or acetone, it may yield a small proportion of one of these compounds in a pure state, but the subsequent deposits consist of mixtures of these two substances, the separation of which is a very troublesome matter. Perhaps the simplest method is that already described. The mixture is slowly crystallised from ethyl acetate at the ordinary temperature, and as soon as a deposit of large crystals has been produced the mother liquor is decanted and the beaker containing the deposit is heated on the water-bath for a few minutes; the transparent crystals, which consist of trianhydrotrisdiphenylsilicanediol, are then separated mechanically from those which have become opaque, and the latter, which consist of tetra-anhydrotetrakisdiphenylsilicanediol, or of the mixture melting at about 184°, are redissolved. These operations are repeated until the trianhydrotrisdiphenylsilicanediol has been separated so far as possible, and the impure tetra-anhydrotetrakisdiphenylsilicanediol which remains is then repeatedly recrystallised from hot acetone until its melting point rises to 200—201°.

The facts recorded in this series of papers (Part XVI. to XIX.) have an important bearing on the views which may be held regarding the structures of many of the inorganic derivatives of silicon; this matter will be discussed in a future communication.

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CCXXV.—*Organic Derivatives of Silicon. Part XVIII. Dibenzylsilicanediol and its Anhydro-derivative.*

By Robert Robison, B.Sc., Ph.D., and
Frederic Stanley Kipping.

In a previous communication on some benzyl derivatives of silicane (Trans., 1908, **93**, 441) the authors described an apparent example of isomerism for which no reasonable explanation could be advanced. By the decomposition of dichlorodibenzylsilicane with water, two compounds were obtained; the one melted at 101°; the other melted at 76°, indefinitely, and was identical with the compound previously prepared by Dilthey, and described by him under the name "dibenzylsilicol" (*Ber.*, 1905, **38**, 4132).

As the results of analyses and molecular-weight determinations seemed to show that both these compounds had the molecular formula $C_{14}H_{16}SiO_2$, and as both could be converted into a "termolecular dibenzylsilicone," they were provisionally regarded as being isomeric, and were distinguished as "α-dibenzylsilicol" and "β-dibenzylsilicol" respectively.

At that time the observations which had been made failed to give any explanation of the supposed isomerism; the possibility of regarding the β-compound as unimolecular dibenzylsilicone, crystallised with one molecule of water, was considered, but was rejected as not being in harmony with the results of our molecular-weight determinations.

The investigation of these compounds was continued by one of us during a few weeks, and later on Dr. Martin took part in the work. Although the latter did not succeed in throwing much light on the subject (*Ber.*, 1912, **45**, 403; compare also footnote, this vol., p. 2108), he found that when the β-compound was dissolved in alcoholic potassium hydroxide, it gave a solution from which the α-silicol was precipitated on the addition of an acid.

In the hope that compounds, analogous to the two dibenzyl derivatives, would be obtained by the hydrolysis of other dichloro-derivatives of alkyl- or aryl-substituted silicanes, we first studied the action of water and alkalis on dichlorophenylbenzylsilicane, dichlorobenzylethylsilicane, and dichlorophenylethylsilicane. The results of this investigation are communicated later, but in the meantime it may be stated that isomeric dihydroxy-compounds were not obtained from any of these three compounds, nor by the hydrolysis of dichlorodiphenylsilicane (compare Kipping, this vol., p. 2108). From diphenylsilicanediol and from phenylethylsilicanediol, however, under suitable conditions, we obtained anhydro-derivatives or oxides of the constitution $HO{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}OH$ and $HO{\cdot}SiPhEt{\cdot}O{\cdot}SiPhEt{\cdot}OH$ respectively; the study of these compounds, combined with a further examination of the two dibenzyl derivatives, led to the following explanation of the relationship between the supposed isomerides.

"α-Dibenzylsilicol" (m. p. 101°) is a dibenzylsilicanediol of the constitution $Si(CH_2{\cdot}C_6H_5)_2(OH)_2$. "β-Dibenzylsilicol" (m. p. 76°), the compound described by Dilthey as dibenzylsilicol (*loc. cit.*), is an anhydro-derivative or oxide of dibenzylsilicanediol, crystallised with one molecule of water; that is to say, this compound has the constitution $HO{\cdot}Si(CH_2{\cdot}C_6H_5)_2{\cdot}O{\cdot}Si(CH_2{\cdot}C_6H_5)_2{\cdot}OH,H_2O$, and is now named anhydrobisdibenzylsilicanediol (compare this vol., p. 2107).

The facts on which we base these conclusions are as follows: The primary product of hydrolysis of dichlorodibenzylsilicane with water or a dilute aqueous solution of ammonium hydroxide is dibenzylsilicanediol (m. p. 101°); this substance is also precipitated on the addition of acetic acid or hydrochloric acid to the solution obtained by hydrolysing the dichloro-compound with a dilute aqueous solution of potassium hydroxide.

When dibenzylsilicanediol is heated at 110°, it loses approximately half a molecule of water and is converted into an oil; this oil absorbs water and gives the compound melting at about 76° (β-dibenzylsilicol), but it also contains a little of the "termolecular silicone" (trianhydrotrisdibenzylsilicanediol). A very similar result is obtained by treating dibenzylsilicanediol (m. p. 101°) with acetyl chloride in ethereal solution; the product is an oil which gives "β-dibenzylsilicol" on exposure to moist air.

"β-Dibenzylsilicol" may also be obtained by treating dibenzylsilicanediol with hydrochloric acid under suitable conditions, but a much larger proportion of the product consists of the "termolecular silicone" when this reagent is employed.

Quantitative experiments with "β-dibenzylsilicol" (m. p. 76°) showed that when this compound was heated at 110° for twenty minutes the loss in weight was exactly equal to that required for the dehydration of a compound of the composition $C_{28}H_{30}O_3Si_2,H_2O$. The oily product, like that obtained from dibenzylsilicanediol, was extraordinarily hygroscopic, and on exposure to the air it gained in weight by an amount practically equal to the previous loss, giving "β-dibenzylsilicol" apparently in a pure condition.

Now from these results it would seem almost certain that the oil obtained by heating the β-compound must have the composition $2C_{14}H_{16}O_2Si - H_2O$, and be identical with the oil formed by heating dibenzylsilicanediol, or treating it with acetyl chloride (or rather with the main component of this oily mixture), for both oils give the same product on exposure to moist air. In all probability, therefore, this oil is an anhydrobisdibenzylsilicanediol of the constitution $HO\cdot Si(CH_2\cdot C_6H_5)_2\cdot O\cdot Si(CH_2\cdot C_6H_5)_2\cdot OH$, and is analogous to the anhydro-derivatives of diphenylsilicanediol and phenylethylsilicanediol, which have been previously mentioned.

If this conclusion is correct, there are two possible ways of conceiving the addition of water to such an anhydro-compound: (*a*) One molecule of water may be taken up, without the occurrence of hydrolysis, giving a hydrated compound, $C_{28}H_{30}O_3Si_2,H_2O$; (*b*) hydrolysis may occur with formation of two molecules of dibenzylsilicanediol.

Considering first the latter possibility, it seems extremely improbable that an oxide or anhydro-compound of the constitution just given would be hydrolysed by cold water. The various compounds of this type which are now known are relatively stable, and, although they are hydrolysed by alcoholic potassium hydroxide without difficulty, apparently they are not acted on by water. Further, if hydrolysis occurred, the compound melting at 76° would presumably have the constitution $Si(CH_2{\cdot}C_6H_5)_2(OH)_2$, and be identical with the dibenzylsilicanediol, which is actually produced when the oxide is hydrolysed with alcoholic potassium hydroxide and the potassium derivative is then decomposed with an acid.

As the possibility of hydrolysis is thus excluded, the alternative explanation is that the anhydro-compound or oxide of the above constitution takes up one molecule of water of hydration. Although it certainly was not to be anticipated that a substance like the oxide in question would be so very hygroscopic and give hydrated crystals, this unexpected behaviour affords no grounds for doubting a conclusion which is supported by so many facts. The indefinite melting point of the crystals corresponds with the view that they are hydrated; also the observation that when the crystals are placed in cold chloroform or benzene they seem to lose water immediately and pass into an oil, which then dissolves, leaving a faint turbidity, due to minute drops of water.

The results of the molecular-weight determinations, which were given previously (*loc. cit.*), can also be satisfactorily explained on the assumption that the crystals melting at 76° are hydrated. In acetic acid solution the values obtained were 260 and 263, whereas in benzene solution they were 540 and 560. A compound of the composition $C_{28}H_{30}O_3Si_2,H_2O$ would have a molecular weight of 488, but in acetic acid solution the water of hydration would doubtless behave as dissolved water, so that the observed molecular weight should equal half the calculated value and be only 244. In benzene solution the same dehydration would take place, but as the water would not dissolve in the benzene to an appreciable extent, it would not affect the freezing point of the solvent very greatly, and an observed molecular weight of about 470 might be expected; moreover, judging from analogy to other similar silicon compounds, the oxide or anhydride itself would probably be associated, so that the values 540 and 560 actually found are what might have been anticipated.

Finally, it may be pointed out that under those conditions which lead to the production of "β-dibenzylsilicol" from dibenzylsilicanediol, a certain proportion of the "termolecular silicone" is always produced. This fact is readily understood if the formation of both compounds is a process of condensation. In the one case, two molecules condense with elimination of one molecule of water; in the other, three molecules condense with elimination of three molecules of water.

The one fact, which at present seems to be a little at variance with the above conclusion, is that when anhydrobisdibenzylsilicanediol is heated strongly it does not yield any "quadrimolecular silicone," as might have been expected from the behaviour of anhydrobisdiphenylsilicanediol (this vol., p. 2133), but is converted into the "termolecular silicone" already described.

As redeterminations of the molecular weight of this compound only served to confirm the previous conclusion that it had the molecular formula $[Si(CH_2{\cdot}C_6H_5)_2O]_3$, it must be assumed that, at the high temperature which is required to bring about any change in anhydrobisdibenzylsilicanediol, both hydrolysis and condensation occur. This assumption is not inherently improbable, and is not altogether unsupported by experimental evidence (compare this vol., p. 2133); consequently, we have little hesitation in concluding that Dilthey's "dibenzylsilicol" is a hydrated form of anhydrobisdibenzylsilicanediol.

EXPERIMENTAL.

Preparation of Dibenzylsilicanediol, $Si(CH_2{\cdot}C_6H_5)_2(OH)_2$.

In our earlier experiments on the hydrolysis of dichlorodibenzylsilicane (*loc. cit.*) the results were very uncertain; in some cases we obtained "α-dibenzylsilicol" (m. p. 101°), in others the β-compound, or a mixture of the two, and, as a rule, a considerable proportion of the dichloride was converted into a viscid oil. It was therefore necessary, in the first place, to ascertain which of these substances was the primary product of hydrolysis and to find the conditions under which it was formed. For this purpose we examined the behaviour of the dichloride towards water, and towards aqueous solutions of ammonium hydroxide and potassium hydroxide.

When the finely divided dichloride was merely left exposed to atmospheric moisture, hydrogen chloride was rapidly evolved, and the transparent crystals soon became white and opaque; in the course of about twenty-four hours there had been formed a pasty mass, which then slowly hardened on further exposure to the air. This product was practically free from dibenzylsilicanediol, as it did not dissolve to an appreciable extent in a 5 per cent. aqueous solution of potassium hydroxide; it consisted principally of trianhydrotrisdibenzylsilicanediol, but also contained some anhydrobisdibenzylsilicanediol.

When the crystalline dichloride was mixed with ether in sufficient quantity to give a liquid, and the latter was slowly dropped into cold water, the dichloride was rapidly decomposed, with a slight development of heat, giving a somewhat pasty solid; with small quantities of the dichloride, this method of hydrolysis gave a fairly good yield of dibenzylsilicanediol, but with quantities of 10 grams or more the operation was not so successful, and the product might be almost free from dibenzylsilicanediol; this was probably because the pasty solid, when separated by filtration, still contained some unchanged dichloride, which would give rise to hydrochloric acid, and thus cause the condensation of the diol.

Better results were obtained when the dichloride was liquefied by gently warming it, and was then dropped into a cold 4 per cent. aqueous solution of ammonium hydroxide, the latter being well stirred during the operation. The product was a white solid, which, after having been repeatedly washed with water, was dried on porous earthenware, and then washed with a little light petroleum in order to free it from traces of dibenzyl. Such preparations sintered at about 93°, melted completely at about 96°, and consisted almost entirely of dibenzylsilicanediol, but they were not completely soluble in a 5 per cent. aqueous solution of potassium hydroxide.

In later experiments the melted dichloride was dropped slowly into a 5 per cent. aqueous solution of potassium hydroxide, which was vigorously stirred during the operation. The oil first turned into a white solid, which then slowly dissolved, giving a somewhat turbid solution. The very small proportion of insoluble matter, which probably consisted of dibenzyl, was removed by filtration, after the solution had been shaken well with animal charcoal, and the clear filtrate was rendered slightly acid with acetic acid. The bulky, flocculent precipitate was separated, carefully washed with water, and pressed on porous earthenware, but, like the precipitate of diphenylsilicanediol, obtained in a similar manner, it retained a very large proportion of water, even after several days' exposure to the air; after having been washed with light petroleum, it usually melted at about 98—100°, and consisted of almost pure dibenzylsilicanediol, but contained a very small proportion of matter, insoluble in potassium hydroxide solution.

It would seem, therefore, that this diol, like diphenylsilicanediol, undergoes some decomposition after it has been precipitated from the solution of its potassium derivative; this is no doubt due to the presence of traces of alkali which are adsorbed by the somewhat colloidal precipitate.

The small proportion of impurity contained in the dibenzylsilicanediol prepared by either of the last two methods, is not easily removed. If the impure substance is dissolved in ether and reprecipitated with light petroleum, it is obtained in the form of a cotton-wool-like mass, and by repeating these operations many times, a preparation, which is completely soluble in potassium hydroxide solution, may be isolated. A better method of purification, however, is the following: The impure diol is dissolved in acetone, and water is added to the solution until a turbidity is produced; the solution is then left to evaporate spontaneously. At first the liquid becomes milky, owing to the separation of an oil, but later on, long, silky, opaque needles are deposited. These crystals are easily freed from the milky mother liquors by decantation, and are again dissolved in acetone. The solution now becomes only slightly milky when water is added to it, and the needles form more rapidly than before. These operations are repeated, if necessary, until a portion of the preparation is completely soluble in a 5 per cent. aqueous solution of potassium hydroxide.

When this method is used it is essential that the crystallisation should be completed as rapidly as possible, since the diol undergoes decomposition in aqueous acetone solution with the separation of an oil. For this reason it is best to treat small quantities of the substance at a time, and to avoid the use of more acetone than is necessary. If the sample contains a large proportion of impurity, a preliminary treatment by the first method of purification is advisable.

Dibenzylsilicanediol melts, as previously stated, at 101° when it is quickly heated. It is appreciably soluble in warm water, and separates from the cold solution in long, white filaments; if, however, the solution is heated at about 90° for a short time, it becomes turbid, an oil separates, and the diol seems to be completely decomposed. A similar change seems to occur, but more rapidly, when the aqueous solution of the diol is warmed with a little hydrochloric acid. The solution in potassium hydroxide also becomes turbid when it is heated, and an oil separates.

Effect of Heat on Dibenzylsilicanediol.

In our first paper on these dibenzyl compounds we stated that very indefinite results had been obtained in studying the effect of heat on dibenzylsilicanediol (α-dibenzylsilicol). We therefore made a series of quantitative experiments in order, if possible, to discover what changes are undergone by the diol at various temperatures.

In these experiments the pure compound was heated in a weighing bottle, and the loss in weight was ascertained at short intervals. It was thus found that at 105—112° the weight became relatively constant after thirty to fifty minutes;

0·6608, in thirty minutes at 110—112°, lost 0·0292, or 4·42 per cent.

0·5351, in fifty minutes at 105—110°, lost 0·0229, or 4·28 per cent.

The loss of $\frac{1}{2}$ mol. of water by a compound of the composition $Si(CH_2{\cdot}C_6H_5)_2(OH)_2$ would mean a loss of 3·68 per cent.

When the heating was continued after this stage had been reached, a further very gradual loss in weight occurred, but even after many hours there was no indication of a constant weight being reached. Very similar results were obtained when the diol was heated at about 130°; during the first twenty minutes a rapid loss in weight, amounting to about 4·6 per cent., took place, and after this stage the weight slowly and continuously diminished, without any sign of becoming constant.

The oily product, which is obtained when the diol is heated at about 110°, consists essentially of anhydrobisdibenzylsilicanediol; when it is treated with cold alcohol, it passes almost entirely into solution, leaving only a very slight, viscid residue, which probably consists of the impure "termolecular silicone." The alcoholic solution gives with water an oily precipitate, which, when dissolved in light petroleum, yields a crystalline deposit of hydrated anhydrobisdibenzylsilicanediol.

The oily residue obtained when the diol is heated at about 130° is also a mixture. On treatment with alcohol it yields an insoluble portion, from which the "termolecular silicone" can be isolated by recrystallisation from light petroleum. The soluble portion, which is probably a mixture of anhydrobisdibenzylsilicanediol and other condensation products, could not be separated into its components.

From the results of these experiments it would seem that dibenzylsilicanediol decomposes at about 110°, giving anhydrobisdibenzylsilicanediol as principal product; as, however, the "termolecular silicone" is also produced in small quantities, the loss in weight is more than that required for the formation of the first-named compound. The slow loss in weight which continues to occur after these anhydro-derivatives have been formed, seems to be due in part to the formation, by atmospheric oxidation, of benzaldehyde, and the subsequent volatilisation of this product.

It is obvious, however, that the effect of heat on dibenzylsilicanediol is to bring about a series of reactions; although at 110° the main product is anhydrobisdibenzylsilicanediol, at higher temperatures a large proportion of the "termolecular silicone" is formed.

Action of Hydrochloric Acid and of Acetyl Chloride on Dibenzylsilicanediol.

Dibenzylsilicanediol, like diphenylsilicanediol, is readily acted on by hydrochloric acid, even at the ordinary temperature, and when this acid is used to precipitate the diol from solutions of its alkali derivatives, the precipitate must be very carefully washed, otherwise it may gradually undergo decomposition, giving a glue-like mass. As a rule, the principal product of the action of hydrochloric acid is the "termolecular silicone," but in certain circumstances anhydrobisdibenzylsilicanediol is also formed. If, for example, a drop of concentrated hydrochloric acid is added to an ethereal solution of the pure diol, and the solution is kept during twenty-four hours and then allowed to evaporate, it leaves an oil, which is a mixture of the "termolecular silicone" with a small proportion of anhydrobisdibenzylsilicanediol. If, on the other hand, the pure diol is dissolved in alcohol containing a little concentrated hydrochloric acid, in a short time pure crystals of the "termolecular silicone" are deposited, and the quantity of this deposit continues to increase during many days; this seems to be the most convenient method for the preparation of the last-named compound, and the yield is very good; small quantities of anhydrobisdibenzylsilicanediol seem to be the only by-product. The diol is also slowly and apparently quantitatively converted into the "termolecular silicone" when it is exposed to the fumes of hydrochloric acid in a closed vessel.

In our previous paper we stated that dibenzylsilicanediol (α-dibenzylsilicol) could be recovered unchanged from its solution in acetyl chloride; further investigation has shown, however, that the results of the action of acetyl chloride vary very considerably with the conditions of the experiment. When the pure diol is dissolved in a small quantity of the acid chloride, and the solution is rapidly evaporated in an exhausted desiccator containing potassium hydroxide (as was done in the experiment previously recorded), the residue consists largely, if not entirely, of the original diol. If, however, the solution is allowed to evaporate spontaneously, it deposits an oil, which consists of a mixture of anhydrobisdibenzylsilicanediol and unchanged dibenzylsilicanediol.

Many attempts were made to convert the diol quantitatively into anhydrobisdibenzylsilicanediol with the aid of acetyl chloride, but the results were very variable; when, for example, a solution of the diol in dry ether was treated with a few drops of acetyl chloride, left for about six hours, and then evaporated over potassium hydroxide at the ordinary temperature, it always gave an oil, but this oil varied in composition. In some cases, when dissolved in a mixture of ether and light petroleum, the oil gave a good yield of the hydrated crystals of anhydrobisdibenzylsilicanediol; in others, it gave crystals of the "termolecular silicone," which might or might not be mixed with the hydrated crystals of anhydrobisdibenzylsilicanediol. It is, perhaps, desirable to add that the hydrated crystals were never formed until the oil, which contained anhydrobisdibenzylsilicanediol, had been exposed to atmospheric moisture or crystallised from solvents containing traces of water.

Anhydrobisdibenzylsilicanediol, $HO\cdot Si(CH_2\cdot C_6H_5)_2\cdot O\cdot Si(CH_2\cdot C_6H_5)_2\cdot OH$.

It has been shown above that anhydrobisdibenzylsilicanediol is formed when dibenzylsilicanediol is heated alone, or treated with hydrochloric acid or acetyl chloride, two molecules of the diol undergoing condensation with loss of one molecule of water. Although, theoretically, this change appears to be a very simple one, as a matter of fact it is by no means easy to bring it about quantitatively, and the yield of the anhydro-compound is always very unsatisfactory.

As a result of many experiments, the following was found to be the best method of preparation: Dibenzylsilicanediol (3 grams) is dissolved in dry ether (20 c.c.), acetyl chloride (30 drops) is added, and the solution, contained in a beaker, is kept in a desiccator over potassium hydroxide during three hours. The desiccator is then exhausted in order to get rid of as much acetyl chloride as possible. After about six hours, small crystals of the "termolecular silicone" usually begin to form at the surface of the liquid; the solution is then poured into excess of a cooled, dilute aqueous solution of ammonium hydroxide, with which it is thoroughly shaken. The product is next extracted with ether, the extract is evaporated, and the oily residue is stirred with a little alcohol, which causes the immediate separation of a crystalline precipitate, consisting of slightly impure "termolecular silicone." The filtered alcoholic solution is diluted with water, and the inside of the beaker is vigorously rubbed with a glass rod; the hydrated crystals of anhydrobisdibenzylsilicanediol, which are then deposited, are separated and dried on porous earthenware. The crystalline product is now dissolved in ether, the solution is diluted with a large volume of light petroleum, rapidly filtered, and allowed to evaporate spontaneously. After a short time, the crystals of the hydrated compound are deposited in a pure state; they are washed with light petroleum, spread on porous earthenware, and left in a desiccator over paraffin shavings. Under the conditions just described, about 2 grams of the hydrated anhydrobisdibenzylsilicanediol and 0·9 gram of the "termolecular silicone" are obtained from 3 grams of dibenzylsilicanediol.

The analyses of his "dibenzylsilicol," given by Dilthey (*loc. cit.*), and also those which were recorded in our former paper, did not agree very well with the calculated values, as the percentage of carbon was always a little too high; we therefore analysed a specimen prepared in the above manner, and obtained the following results:

0·1692 gave 0·4272 CO_2 and 0·1000 H_2O. C=68·9; H=6·6.
0·1683 ,, 0·4265 CO_2 ,, 0·1002 H_2O. C=69·1; H=6·6.
0·4248 ,, 0·1042 SiO_2. Si=11·5.
$C_{28}H_{30}O_3Si_2,H_2O$ requires C=68·7; H=6·5; Si=11·6 per cent.

The percentage of carbon is again rather too high, and it would seem, therefore, that the hydrated crystals very readily lose a small proportion of their water.

As regards the outward properties of this hydrated compound, we have little to add to our previous description. The somewhat indefinite melting point of the compound is now accounted for, and also the formation of traces of oily matter when the substance is recrystallised from anhydrous solvents. The hydrated compound is readily soluble in cold chloroform or benzene, and, as the crystals dissolve, the solvent becomes turbid, owing to the separation of the water of hydration; when such solutions are heated it can be seen that water is expelled, and on subsequent evaporation they give an oil, which gradually crystallises on exposure to atmospheric moisture.

The hydrated crystals seem to be unchanged by cold dilute potassium hydroxide solution, but, as observed by Martin (*loc. cit.*) they dissolve in alcoholic potassium hydroxide, giving a solution from which acids precipitate dibenzylsilicanediol. This change is not a conversion of one isomeride into another, as was supposed by Martin, but is a process of hydrolysis, which may also be brought about with the aid of a solution of potassium hydroxide in aqueous acetone.

Effect of Heat on the Hydrated Crystals of Anhydrobisdibenzylsilicanediol.

If the compound just described is, in fact, a hydrated form of anhydrobisdibenzylsilicanediol, it should in all probability lose its water at 100°.

Now in our previous paper (*loc. cit.*) we stated that after about seventy hours' heating at 100° this compound ("β-dibenzylsilicol") lost 6·6 per cent. in weight, whereas the theoretical loss for a substance of the composition $C_{28}H_{30}O_3Si_2,H_2O$ is 3·68 per cent.

The further study of this matter showed that, in the experiment just referred to, the most important fact had escaped observation, because the loss in weight had not been determined after a sufficiently short interval. When the hydrated crystals are heated at 100—110° during successive periods of about ten minutes, and the loss in weight is determined after each period, it is found that a very definite stage is rapidly reached, corresponding with the theoretical loss of 3·68 per cent.; after this loss has occurred, the diminution in weight during further periods of ten minutes at 100—110° is so small that successive weighings do not differ by more than about 0·0001 gram.

The following results were thus obtained:

I. 0·7698 at 100—110° during twenty minutes lost 0·0288 or 3·74 per cent.

II. 0·8805 at 100—110° during twenty-two minutes lost 0·0324 or 3·68 per cent.

III. 0·6678 at 105—110° during seventeen minutes lost 0·0241 or 3·61 per cent.

Experiments carried out at higher temperatures (130—150°) showed that a loss in weight of about 3·7 per cent. occurred during the first ten minutes, and thereafter a very slow and continuous decrease set in, the loss amounting to 7·8 per cent. at the end of two hours. This slow and continuous loss which occurs after the water has been expelled seems to be due, as in the case of dibenzylsilicanediol, to the volatilisation of benzaldehyde, which is formed by atmospheric oxidation; the odour of this aldehyde becomes more and more pronounced as the heating is prolonged.

The oil which remains when the hydrated crystals have lost the theoretical quantity of water doubtless consists of practically pure anhydrobisdibenzylsilicanediol, but we have not been able to obtain it in a crystalline condition, possibly because it is so very hygroscopic. When the oil is kept in a closed vessel it shows no signs of crystallising, but when it is exposed to the air, if only for a few moments, crystals subsequently begin to form at the surface; the hydrated crystalline compound is also obtained in a pure state when the oil is dissolved in light petroleum, and the solution is allowed to evaporate spontaneously in the air.

That the formation of the crystalline compound is due to the absorption of water was also proved quantitatively. The oil obtained in experiment I (see above) by heating 0·7698 gram of the hydrated compound, was exposed to atmospheric moisture and weighed from time to time; it gradually changed to a crystalline mass, the increase in weight taking place more and more slowly, until at the end of twenty-one days' time the weight of the hydrated crystals was 0·7677 gram.

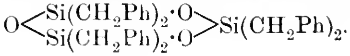
Treatment of Anhydrobisdibenzylsilicanediol with Acetyl Chloride.

In our experiments on the behaviour of dibenzylsilicanediol towards acetyl chloride, we found that the proportion of "termolecular dibenzylsilicone" seemed to increase with the proportion of the chloride which was used, and with the time during which the treatment was prolonged. It seemed, therefore, very probable that the hydrated crystals of anhydrobisdibenzylsilicanediol might give a quantitative yield of the "termolecular silicone" with excess of this acid chloride. This expectation proved to be unfounded. When the hydrated compound is treated with the acid chloride a fairly vigorous reaction takes place, owing doubtless to the presence of the water of hydration, but when the solution is afterwards evaporated over potassium hydroxide in a desiccator, it gives an oil, which has the properties of anhydrobisdibenzylsilicanediol, and which, on exposure to moist air, gives the original hydrated crystals. The same result is obtained when the hydrated compound is heated with acetyl chloride, and in no case did we observe the formation of the "termolecular silicone."

It must be inferred, therefore, that the formation of the "termolecular silicone" during the interaction of acetyl chloride and dibenzylsilicanediol is due to the condensation of anhydrobisdibenzylsilicanediol with dibenzylsilicanediol, and not to the action of the chloride on the first-named compound.

Anhydrobisdibenzylsilicanediol, in the solid state, is also stable towards hydrogen chloride; when either the hydrated crystals or the anhydrous compound is exposed to the fumes of the acid during several days, no appreciable change occurs.

Trianhydrotrisdibenzylsilicanediol,



$$O<\begin{matrix}Si(CH_2Ph)_2\cdot O\\ Si(CH_2Ph)_2\cdot O\end{matrix}>Si(CH_2Ph)_2.$$

Although the "termolecular dibenzylsilicone" (trianhydrotrisdibenzylsilicanediol, compare this vol., p. 2107) does not seem to be formed by the action of acetyl chloride on anhydrobisdibenzylsilicanediol, it may be obtained, as previously stated (*loc. cit.*), by strongly heating the last-named compound alone, and then treating the residue with acetic anhydride; the use of acetic anhydride, in fact, is unnecessary, as the "termolecular silicone" may be produced by merely heating anhydrobisdibenzylsilicanediol at a sufficiently high temperature (250°) during about ten minutes. The results of this treatment, however, are very uncertain, and we have not ascertained the conditions under which the transformation is best accomplished.

It is obvious, nevertheless, that if the original compound and the product have, respectively, the constitutions assigned to them, the conversion of the one into the other is not a simple process. In view of the possibility that the substance hitherto regarded as being the "termolecular silicone" might really be the "quadrimolecular silicone," produced by the condensation of two molecules of anhydrobisdibenzylsilicanediol, we made some further determinations of its molecular weight, but the results only confirmed those previously recorded.

Ebullioscopic Method.

0·7860 in 11·0 c.c. chloroform gave E = 0·295. M.W. = 630.
0·7860 ,, 12·9 ,, ,, ,, E = 0·225. M.W. = 704.

Cryoscopic Method.

0·3135 in 14·35 benzene gave $\Delta t = -0{\cdot}167$. M.W. = 641.
0·5230 ,, 14·35 ,, ,, $\Delta t = -0{\cdot}285$. M.W. = 627.
0·7130 ,, 14·35 ,, ,, $\Delta t = -0{\cdot}387$. M.W. = 630.
$[Si(CH_2{\cdot}C_6H_5)_2O]_3$ requires M.W. = 679.

Although the "termolecular silicone" is practically insoluble in alcohol, it is slowly dissolved by an alcoholic solution of potassium hydroxide, and is converted into the potassium derivative of dibenzylsilicanediol; the hydrolysis of the silicone will be further studied.

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CCXXVI.—*Organic Derivatives of Silicon. Part XIX. The Preparation and Properties of Some Silicanediols of the Type* $SiR_2(OH)_2$.

By Robert Robison, B.Sc., Ph.D., and
Frederic Stanley Kipping.

During the progress of the experiments recorded in the preceding paper we began the investigation of some other dichlorides in the expectation of obtaining from them products of hydrolysis corresponding with those derived from dichlorodibenzylsilicane. The compounds selected for this purpose were dichlorobenzylethylsilicane and dichlorophenylethylsilicane, both of which had been previously described (Kipping, Trans., 1907, **91**, 215, 721). From each of these dichlorides a product of hydrolysis had already been prepared; dichlorophenylethylsilicane, when decomposed with water without any special precautions being taken, gave an oil which was called phenylethylsilicone, but which was not investigated (Kipping, Trans., 1907, **91**, 218); dichlorobenzylethylsilicane, under similar conditions, gave an oil, benzylethylsilicone, which was studied in some detail by Robison and Kipping (Trans., 1907, **93**, 442).

From the knowledge which we now have, that the hydrolysis of such dichlorides often leads to the formation of a complex mixture of products, it would seem that the oily silicones just referred to may not have been pure compounds, and that the benzylethylsilicone, to which, from the results of molecular-weight determinations, we assigned the formula $[SiEt(CH_2{\cdot}C_6H_5)O]_3$, may possibly have contained other condensation products of benzylethylsilicanediol, having structures analogous to those of the compounds derived from diphenylsilicanediol (this vol., p. 2125).

Whether this be the case or not, in the experiments now to be described the object was to isolate the primary product of the hydrolysis of the dichloride in the first instance, and for this purpose the decomposition was very cautiously brought about with the aid of cold dilute ammonium hydroxide solution. Under these conditions, *benzylethylsilicanediol*, $SiEt(CH_2{\cdot}C_6H_5)(OH)_2$, and *phenylethylsilicanediol*, $SiEtPh(OH)_2$, were obtained without much difficulty from the corresponding dichlorides.

These crystalline compounds are much more readily soluble in water than are the diphenyl- and dibenzyl-silicanediols, and, like these two diols, they give soluble derivatives with a solution of potassium hydroxide; they are both readily decomposed by traces of hydrochloric acid and by other reagents, but in most cases the products are oils, from which, so far, only one crystalline compound has been isolated. Judging from analogy, these oils consist of mixtures of condensation products of the diol similar to that obtained from diphenylsilicanediol under various conditions, but as the components of these mixtures have doubtless much lower melting points than the corresponding derivatives of diphenylsilicanediol, they cannot be isolated by the methods which were found to be of service in the case of the latter compounds.

The one condensation product which has been obtained in quantities sufficient to enable us to determine its composition is derived from two molecules of phenylethylsilicanediol, and is an anhydrobisphenylethylsilicanediol of the constitution

$$HO\cdot SiPhEt\cdot O\cdot SiPhEt\cdot OH;$$

this compound, therefore, is analogous to the corresponding derivatives of diphenylsilicanediol and dibenzylsilicanediol, which have already been described (this vol., pp. 2131, 2151).

In addition to the dichlorides already mentioned, we prepared dichlorophenylbenzylsilicane, and examined its products of hydrolysis; experiments on these lines had already been made by one of us in conjunction with Dr. Martin, but the work had not been completed, and none of the products had been analysed. The results were very similar to those obtained in the case of the phenylethyl and benzylethyl derivatives; when hydrolysed with a cold solution of ammonium hydroxide, the dichloride gave a crystalline *phenylbenzylsilicanediol*, $SiPh(CH_2\cdot C_6H_5)(OH)_2$, which was easily decomposed by acids and various other reagents, but so far we have been able to isolate only small quantities of crystalline condensation products from the oils which are thus produced.

As some five disubstituted dichlorosilicanes have now been hydrolysed, and in all cases it has been possible to obtain the corresponding dihydroxy-compound of the type $SiR_2(OH)_2$, it would seem that silicon derivatives of this kind are much more stable than the corresponding compounds of carbon.

Several striking and unexpected differences in behaviour have been met with in studying these compounds, more particularly with regard to their decomposition by heat; thus, whereas diphenylsilicanediol is readily and for the most part transformed into trianhydrotrisdiphenylsilicanediol, dibenzylsilicanediol gives as principal product anhydrobisdibenzylsilicanediol; and whereas anhydrobisdiphenylsilicanediol undergoes condensation, giving tetra-anhydrotetrakisdiphenylsilicanediol, anhydrobisdibenzylsilicanediol seems to give no corresponding compound.

It is also noteworthy that in the case of every diol, the result of the application of heat seems to be the formation of two or more condensation products, and, in some instances at least, the mixture of compounds which is thus formed undergoes no further change under the given conditions; it appears, therefore, that two or more reactions which are not successive stages of dehydration occur simultaneously from the outset.

EXPERIMENTAL.

Phenylethylsilicanediol, $SiPhEt(OH)_2$.

Dichlorophenylethylsilicane, prepared by the method previously described, and freed from diphenyl as far as possible by repeated distillation under diminished pressure (Kipping, Trans., 1907, **91**, 215), is dissolved in pure, dry ether, and the solution is slowly dropped into an ice-cold, dilute solution of ammonium hydroxide, which is vigorously stirred during the operation. The ethereal layer is then separated, and the ammoniacal solution is extracted three or four times with ether. These solutions deposit the diol in long, transparent needles when they are evaporated at the ordinary temperature, but, as the original ethereal layer gives a product which contains a considerable proportion of oily impurity, whilst the later extracts give an almost pure deposit, it is advisable not to mix the solutions together. The product is recrystallised at the ordinary temperature from a mixture of ether and light petroleum, from which it separates in long, colourless needles; it is then washed with light petroleum, and left on porous earthenware in a desiccator containing potassium hydroxide:

0·1712 gave 0·3602 CO_2 and 0·1141 H_2O. C=57·4; H=7·4.
0·1579 „ 0·3310 CO_2 „ 0·1049 H_2O. C=57·2; H=7·4.
0·2047 „ 0·0734 SiO_2. Si=16·8.
$C_8H_{12}O_2Si$ requires C=57·0; H=7·1; Si=16·8 per cent.

Phenylethylsilicanediol melts sharply at 70° when it is heated rather quickly. It dissolves freely in all the common solvents except cold light petroleum, in which it is only very sparingly soluble; it is also moderately soluble in cold water, but it is decomposed when the solution is warmed, and an oil separates. It gives a clear solution of its potassium derivative when it is treated with a cold, dilute solution of potassium hydroxide, and from sufficiently concentrated solutions it is reprecipitated in crystals on the cautious addition of diluted acetic acid.

Phenylethylsilicanediol is the least stable of all the substituted silicanediols which have so far been prepared; specimens purified in the manner described above undergo decomposition in the course of some days when they are kept in a stoppered bottle in a desiccator, and even the most highly purified samples become oily in the course of three or four weeks, being partly transformed into anhydrobisphenylethylsilicanediol (see below).

It also becomes oily and loses the elements of water very rapidly in a dry vacuum, but the results of quantitative experiments seem to show that even under these conditions the change is not a simple one; thus, a sample (0·4797 gram) which was kept in a vacuum over sulphuric acid continued to lose in weight during thirty-one days, at the end of which time the loss amounted to 8·8 per cent., against a theoretical loss of 10·7 per cent. for the change, $SiPhEt(OH)_2 = SiPhEtO + H_2O$. Even then the weight was not quite constant, but when the sample was subsequently heated at 100° during an hour, instead of a further loss, a gain in weight took place, probably the result of atmospheric oxidation. The oily product was insoluble in a solution of potassium hydroxide, and could not be obtained in crystals.

The decomposition of phenylethylsilicanediol at 100° also seems to be a complex change. Samples of about 0·5 gram become practically constant in weight at this temperature in less than two hours, the loss amounting to about 7 per cent.; the product is a very viscid oil, insoluble in a solution of potassium hydroxide.

Phenylethylsilicanediol is extremely sensitive to hydrochloric acid, and in its preparation from the dichloro-derivative as described above, great care must be taken that the stirring arrangement is efficient; otherwise the primary product may be decomposed. When the pure diol is exposed to the fumes of hydrochloric acid, it is completely converted into an oil in the course of half an hour; judging from the behaviour of dibenzylsilicanediol, this oil should consist of trianhydrotrisphenylethylsilicanediol, but unfortunately it could not be brought to crystallise, and therefore was not analysed.

A clear solution of the sodium derivative of phenylethylsilicanediol in excess of a dilute aqueous solution of sodium hydroxide yields an oily precipitate in the course of several weeks when it is kept in absence of air; in open vessels this oily precipitate is formed in the course of a few days, just as in the case of other substituted silicanediols.

Anhydrobisphenylethylsilicanediol, HO·SiPhEt·O·SiPhEt·OH.

This compound is formed when purified samples of phenylethylsilicanediol are kept in a stoppered bottle at the ordinary temperature, but it seems possible that the change is due to the presence of traces of acid or alkali, since very carefully purified specimens undergo decomposition only very slowly. This condensation product is also formed when a solution of the sodium derivative of phenylethylsilicanediol is carefully treated with a slight excess of hydrochloric acid, but it is best prepared by adding a few drops of diluted hydrochloric acid to an aqueous solution of phenylethylsilicanediol and leaving the mixture at the ordinary temperature during about twenty-four hours; the crystalline precipitate is separated, dried on porous earthenware, and recrystallised from boiling light petroleum, with or without the addition of a little ether, when it is obtained in long, transparent needles, melting sharply at 87·5°:

0·1833 gave 0·4072 CO_2 and 0·1170 H_2O. C = 60·6; H = 7·1.
0·1751 ,, 0·3881 CO_2 ,, 0·1120 H_2O. C = 60·4; H = 7·1.
0·2300 ,, 0·0871 SiO_2. Si = 17·8.
$C_{16}H_{22}O_3Si_2$ requires C = 60·3; H = 6·9; Si = 17·8 per cent.

Molecular-weight determinations were made in benzene solution by the cryoscopic method, and in chloroform solution by the ebullioscopic method:

0·213 in 14·4 benzene gave $\Delta t = -0\cdot129$. M.W. = 562.
0·478 ,, 14·4 ,, ,, $\Delta t = -0\cdot256$. M.W. = 635.
0·400 ,, 15·6 ,, ,, $\Delta t = -0\cdot193$. M.W. = 651.
0·475 ,, 9·2 c.c. chloroform gave E = 0·365. M.W. = 368.
0·475 ,, 10·5 ,, ,, ,, E = 0·320. M.W. = 368.
0·475 ,, 13·8 ,, ,, ,, E = 0·260. M.W. = 344.
0·645 ,, 9·6 ,, ,, ,, E = 0·430. M.W. = 406.
0·645 ,, 10·6 ,, ,, ,, E = 0·370. M.W. = 428.
0·645 ,, 13·9 ,, ,, ,, E = 0·315. M.W. = 382.

The results obtained in benzene solution are widely different from the calculated value for the molecular weight, namely, 319, whilst those obtained in chloroform solution agree fairly well with this value, considering the probability that the molecules are associated to some extent even in the boiling solvent. We conclude, therefore, that the compound in question has the structure assigned to it above; from its methods of formation, it might possibly be a dianhydrotrisphenylethylsilicanediol of the constitution

HO·SiPhEt·O·SiPhEt·O·SiPhEt·OH,

which would have a molecular weight of 469, and would contain C = 61·4, H = 6·8, Si = 18·1 per cent.; this possibility, however, seems to be excluded by the results of the analyses and of the molecular-weight determinations in chloroform solution.

Anhydrobisphenylethylsilicanediol is readily soluble in the ordinary solvents, with the exception of light petroleum, but is practically insoluble in water. It does not seem to undergo any decomposition in a vacuum, or at its melting point, and even when it has been heated at 110° and then cooled, it melts at the same temperature as the pure compound. When heated at 150° it loses weight slowly, and in the course of an hour the loss amounts to about 6 per cent., which is more than the quantity required for the change $C_{16}H_{22}O_3Si_2 = C_{16}H_{20}O_2Si_2 + H_2O$; part of this loss may be due to volatilisation, as the oily product still contains a large proportion of the unchanged substance, which may be isolated with the aid of light petroleum.

Anhydrobisphenylethylsilicanediol is also transformed into an oil in the course of a few days when it is left exposed to the fumes of hydrochloric acid, but the product could not be brought to crystallise.

A colourless solid, which, apparently, is the sodium derivative, is almost immediately precipitated in crystals when anhydrobisphenylethylsilicanediol is dissolved in a small proportion of a dilute solution of sodium hydroxide; this solid is hydrolysed by water, giving the original compound. When, however, anhydrobisphenylethylsilicanediol is treated with a larger proportion of the sodium hydroxide solution, this sodium derivative is not precipitated, and the anhydro-compound is hydrolysed; if, after a short time, a slight excess of acetic acid is added, and the solution is extracted with ether, the extract contains phenylethylsilicanediol, which is deposited in crystals when the ether is evaporated at the ordinary temperature.

The mother liquors which are obtained in the purification of anhydrobisphenylethylsilicanediol contain a very small proportion of another crystalline compound, which is isolated only with great difficulty. This compound separates from light petroleum in silky needles, and melts sharply at 81°; when mixed with anhydrobisphenylethylsilicanediol, it gave a mixture which melted at about 70°. It is very readily soluble in ether, alcohol, or other common solvents, but is only sparingly soluble in light petroleum; it gives a soluble derivative with a solution of sodium hydroxide.

Owing to the very small quantity of material available, it was possible to make only one combustion of this substance, and although the results led us to believe that the compound was a dianhydrotrisphenylethylsilicanediol of the constitution

$$HO{\cdot}SiPhEt{\cdot}O{\cdot}SiPhEt{\cdot}O{\cdot}SiPhEt{\cdot}OH,$$

the evidence was not conclusive.

Benzylethylsilicanediol, $SiEt(CH_2{\cdot}C_6H_5)(OH)_2$.

Pure dichlorobenzylethylsilicane (Kipping, Trans., 1907, **91**, 720) is decomposed with an ice-cold aqueous solution of ammonium hydroxide under the conditions described in the preparation of phenylethylsilicanediol; the ethereal layer is then separated, and the ammoniacal solution is extracted three or four times with ether. The combined ethereal solutions are allowed to evaporate spontaneously, and the product, which is deposited in colourless needles, is recrystallised from a mixture of ether and light petroleum and dried in the air:

0·1882 gave 0·4062 CO_2 and 0·1324 H_2O. C=58·9; H=7·8.
0·1789 ,, 0·3874 CO_2 ,, 0·1244 H_2O. C=59·1; H=7·7.
0·1329 ,, 0·0443 SiO_2. Si=15·6.
$C_9H_{14}O_2Si$ requires C=59·2; H=7·7; Si=15·5 per cent.

Benzylethylsilicanediol crystallises from hot benzene or boiling light petroleum in transparent needles, but from aqueous acetone or aqueous alcohol it is deposited in cotton-wool-like masses, resembling those formed by dibenzylsilicanediol under similar conditions. It is appreciably soluble in cold water, more so in hot water, and it dissolves freely in most of the ordinary organic solvents, but it is only sparingly soluble in cold benzene, and practically insoluble in cold light petroleum.

The powdered substance begins to sinter at about 80°, but when the temperature has risen to about 85° the pasty mass solidifies again, and at the same time increases in bulk very considerably; on being further heated, the compound melts at 100°, or at a somewhat lower temperature if heated very slowly. A single large crystal, heated very slowly in a capillary tube, melts at 85° to a clear liquid, which becomes turbid when kept for some time at that temperature. When, however, large crystals are heated in a test-tube, they do not even sinter at 85°; at this temperature the substance begins to increase in bulk, owing to the formation of a mass of small needles at the surface of the large crystals, and on being further heated it melts at 98—100°.

These observations seem to show that benzylethylsilicanediol is dimorphous; that the variable melting point is not due to the loss of the elements of water is proved by the fact that the compound does not lose in weight to any appreciable extent when it is heated at 85° during thirty minutes, and after this treatment it crystallises from a mixture of ether and light petroleum in needles indistinguishable from those of the original preparation.

At the ordinary temperature, benzylethylsilicanediol is stable in air free from acid fumes, but it loses the elements of water in a dry vacuum, and becomes oily in the course of a day or two; quantitative experiments showed that after having been kept during twenty days in a vacuum over sulphuric acid, the substance had lost 5·9 per cent. in weight; although the weight then appeared to be constant, the residual oil still contained some unchanged benzylethylsilicanediol.

At temperatures of about 100° the diol is much more rapidly decomposed, and the residue soon becomes constant in weight, but, as in the case of other compounds of this type, the loss is only about two-thirds of that required for the change $SiR_2(OH)_2 = HO\cdot SiR_2\cdot O\cdot SiR_2\cdot OH + H_2O$, as indicated by the following examples:

0·5262 lost 0·0324 at 100° during three hours; loss = 6·2.
0·8703 „ 0·0595 „ 110° „ half an hour; loss = 6·8.

The theoretical loss for one molecule of water is 9·9 per cent.

The oily products from these experiments were treated with many different solvents, and were also treated with acetic anhydride, acetyl chloride, etc., but they failed to yield any crystalline substance. Many other experiments were also carried out with the object of obtaining a crystalline silicone or other condensation product. An aqueous solution of the pure diol was treated with a drop of hydrochloric acid, but the precipitate which was formed in the course of twenty-four hours was oily, and did not yield a solid on treatment with various solvents. The diol was exposed to the fumes of hydrochloric acid, but the oil into which it was converted in the course of a few hours could not be made to crystallise. Acetyl chloride, either alone or diluted with dry ether, decomposed the diol, giving an oily product, which was insoluble in an aqueous solution of sodium hydroxide.

The behaviour of benzylethylsilicanediol towards solutions of alkali hydroxides is similar to that of phenylethylsilicanediol; when air is excluded, the solution of the alkali derivative remains clear during many days, but when exposed to the air, the solution soon gives an oily precipitate, which is insoluble in a freshly prepared solution of the alkali hydroxide.

Owing to the fact that benzylethylsilicanediol is decomposed so very readily by hydrochloric acid, even at the ordinary temperature, it is probably not possible to obtain the diol by hydrolysing dichlorobenzylethylsilicane with water; when attempts to do so are made, even on a very small scale, the product is an oil, which does not crystallise.

From the results of the experiments previously recorded (Trans., 1907, **93**, 442) we were led to believe that this oil consisted essentially of trianhydrotrisbenzylethylsilicanediol; this view still seems to be tenable, but judging from the complex character of the oils obtained in the investigation of diphenylsilicanediol (this vol., p. 2130), it may be inferred that the above decomposition product of benzylethylsilicanediol is also a mixture of two or more substances.

Dichlorophenylbenzylsilicane, $SiCl_2Ph\cdot CH_2\cdot C_6H_5$.

Dichlorophenylbenzylsilicane was prepared in these laboratories some years ago by the interaction of trichlorobenzylsilicane and magnesium phenyl bromide in ethereal solution (compare Martin, *Ber.*, 1912, **45**, 403, and footnote, this vol., p. 2108), but the yield was unsatisfactory; we therefore tried a different method, namely, the interaction of trichlorophenylsilicane and magnesium benzyl chloride, but there was little to choose between the two processes. In both cases the preparation of the monoaryl compound presents some difficulty, but whereas the yield of trichlorophenylsilicane is only about 15 per cent. of the theoretical, that of trichlorobenzylsilicane may exceed 60 per cent. In consequence of this great difference it is obviously advantageous to prepare the benzyl derivative first, and then to treat the latter with magnesium phenyl bromide in the usual manner. The product is separated from the magnesium salt in the ordinary way, and fractionated under diminished pressure.

A fraction collected between 235° and 240°/100 mm. was analysed and found to contain 24·8 per cent. of chlorine, instead of 26·5 per cent., as required by theory. As diphenyl was probably the only impurity present, and its elimination would have necessitated repeated fractional distillation, accompanied by considerable loss of material, the sample was merely redistilled once under atmospheric pressure; the portion boiling at 316—320° was then used for the preparation of phenylbenzylsilicanediol.

Phenylbenzylsilicanediol, $SiPh(CH_2\cdot C_6H_5)(OH)_2$.

This compound may be obtained by hydrolysing the dichloro-derivative with an aqueous solution of ammonium hydroxide, as described in preceding cases, but as the product always contained a little diphenyl, we found it more convenient to drop the oily dichloride into a 5 per cent. solution of sodium hydroxide, which was vigorously stirred during the operation. The solution was then filtered from diphenyl, and cautiously treated with diluted acetic acid in slight excess; the bulky precipitate of the diol was separated by the aid of the pump and well washed with water.

Even the freshly precipitated product obtained in this way is not quite pure, and leaves a small proportion of residue when it is treated with a dilute solution of an alkali hydroxide; its behaviour, in fact, is similar to that of dibenzylsilicanediol, and its purification is best accomplished by the method described in the case of the last-named compound (p. 2148). The still moist precipitate is dissolved in cold acetone, the solution is diluted with water until it becomes milky, and is then placed aside; the long needles, which are slowly deposited, are separated from the milky mother liquors and again recrystallised from aqueous acetone, these operations being repeated until the crystals cease to give a milky fluid, and are completely soluble in a dilute solution of alkali hydroxide.

The sample for analysis was dried for a short time over sulphuric acid:

0·2061 gave 0·5108 CO_2 and 0·1159 H_2O. C = 67·6; H = 6·2.
0·3487 „ 0·0914 SiO_2. Si = 12·3.
$C_{13}H_{14}O_2Si$ requires C = 67·7; H = 6·1; Si = 12·3 per cent.

Phenylbenzylsilicanediol crystallises in silky needles, resembling those of dibenzylsilicanediol, and its behaviour towards solvents is similar to that of the latter. Its melting or decomposition point varies with the rate of heating; when rapidly heated, it melts at about 106°, but if kept for a sufficient length of time at 90°, it liquefies completely and loses the elements of water. Like dibenzylsilicanediol, it remains unchanged in a dry vacuum.

Quantitative experiments showed that at 100° the weight became constant in the course of five or six hours; the loss then corresponded very closely with two-thirds of that required for one molecule of water:

1·0030 lost 0·0527. Loss = 5·3.
0·6291 „ 0·0335. Loss = 5·3.
1·0169 „ 0·0502. Loss = 5·0.
The change $C_{13}H_{14}O_2Si - H_2O$ requires a loss of 7·8 per cent.

These results are comparable with those obtained with dibenzylsilicanediol and the other diols described in this paper, and from them it must be concluded that the effect of heat is to bring about the formation of a series of condensation products. In the case of phenylbenzylsilicanediol, the product is a very viscid oil, which is insoluble in a solution of sodium hydroxide; unlike that obtained from dibenzylsilicanediol, it does not absorb water from moist air, and although it doubtless contains a considerable proportion of anhydrobisphenylbenzylsilicanediol, we were unable to isolate this compound from the mixture.

In solution, phenylbenzylsilicanediol is readily decomposed by small quantities of hydrochloric acid, giving an oil, which is insoluble in solutions of alkali hydroxides, and only sparingly soluble in alcohol; on the other hand, the pure compound, in a dry state, may be left exposed to the fumes of hydrochloric acid during a week without its undergoing any appreciable change, in which respect it differs from all the other diols, $SiR_2(OH)_2$, which have hitherto been studied. A solution of the sodium derivative of phenylbenzylsilicanediol in excess of alkali hydroxide behaves in the usual manner, and soon becomes turbid on exposure to the air, giving an oil which is insoluble in a dilute aqueous solution of sodium hydroxide.

Numerous attempts were made to prepare from phenylbenzylsilicanediol one of the various condensation products into which it might be converted, but without success. Small quantities of the pure diol were heated at different temperatures, ranging from 100° to 300°, during lengths of time varying from a few minutes to many hours; the oils so obtained were boiled with acetic anhydride or acetyl chloride, or were directly treated with various solvents, but in no case were we able to isolate a crystalline product in quantities sufficient for analysis. The pure diol was also treated directly with acetyl chloride at the ordinary temperature under various conditions; although it was thus readily converted into an oil, the latter could not be made to crystallise.

From all the oily products which are obtained from phenylbenzylsilicanediol under the different conditions mentioned above, the pure diol may be regenerated. For this purpose the oil is dissolved in alcoholic potassium hydroxide; most of the alcohol is then evaporated under diminished pressure, and the remaining solution is diluted with water; the liquid is then filtered from small quantities of oily matter, and treated with dilute acetic acid in slight excess; the precipitate, which consists of slightly impure phenylbenzylsilicanediol, is recrystallised from aqueous acetone in the manner already described.

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Nottingham.

CCXXVII.—*The Interaction of Iodine and Thiocarbamide. The Properties of Formamidine Disulphide and its Salts.*

By Emil Alphonse Werner.

The interaction of iodine and thiocarbamide under different conditions presents several points of peculiar interest which seemed to merit investigation; a careful study of the subject has brought to light a number of interesting facts connected with the mechanism of the change and having a direct bearing on the tautomeric constitution of thiocarbamide.

Storch (*Monatsh.*, 1890, **11**, 452), as the result of his work on the action of a number of different oxidising agents on thiocarbamide in acid solution, has shown that in all his experiments a basic disulphide of the constitution $NH_2C({:}NH)\cdot S\cdot S\cdot C({:}NH)\cdot NH_2$ was produced; quite recently Fichter and Wenk (*Ber.*, 1912, **45**, 1373) have obtained Storch's base by the electrolytic oxidation of thiocarbamide in acid solution, and have called it formamidine disulphide, a name which is adopted throughout the present paper. Iodine is included amongst the oxidising agents employed by Storch in the production of this base, the formation of which he points out furnishes a strong argument in favour of the unsymmetrical formula $NH{:}C(NH_2)\cdot SH$ for thiocarbamide. Formamidine disulphide is a very weak base, and has not been obtained in the free state; addition of alkali, or even sodium acetate, to its salts produces immediate precipitation of sulphur, indicating, in conformity with "Fromm's rule" (*Annalen*, 1906, **348**, 144), the presence of the grouping $-\ddot{C}\cdot S\cdot S\cdot\ddot{C}-$ in its constitution; one of its most characteristic salts, namely, the dinitrate,[*] is almost insoluble in water containing about 5 per cent. of nitric acid, and hence is precipitated in crystalline form when an oxidising agent is added, even to a dilute solution of thiocarbamide containing an excess of this acid. Curiously enough, the method recommended by Storch (*loc. cit.*) for obtaining the best yield of the dinitrate, namely, oxidation by potassium permanganate, has been found to give the poorest result when compared with other oxidising agents, and particularly with iodine. In accordance with the equation:

$$2CSN_2H_4 + O = C_2S_2N_4H_6 + H_2O,$$

the yield of dinitrate should amount to 181 per cent. of the weight of thiocarbamide used; Storch obtained as a maximum from 114 to 123 per cent., a result which has been confirmed by following exactly his directions; on the other hand, yields of 163 and 169·7 per cent. can be easily obtained by oxidation of thiocarbamide by hydrogen peroxide and by nitrous acid respectively in the presence of dilute nitric acid, and the yield by oxidation with potassium permanganate may be raised to 134 per cent. by following the directions given in the experimental part of the paper.

Formamidine disulphide is itself very prone to further oxidation, and hence suffers decomposition during the interaction in propor-

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[*] This compound was originally obtained by McGowan (Trans., 1886, **49**, 195), who assumed it to be a "dithiocarbamide" dinitrate, $(CSN_2H_4)_2(NO_3)_2$, analogous to the compound $(CSN_2H_4)_2Cl_2$, prepared by Claus, and which is really formamidine disulphide hydrochloride.

tion to the reactivity of the oxidising agent used. The production of the base by means of iodine takes place in accordance with the equation:

$$2CSN_2H_4 + I_2 = C_2S_2N_4H_6,2HI;$$

there is no secondary reaction to influence the change, and in the presence of nitric acid, the dinitrate of the base has been obtained to the extent of 180·2 per cent. of the weight of thiocarbamide used, the theoretical yield being 181 per cent.

When iodine solution is added to a neutral concentrated aqueous solution of thiocarbamide, the colour of the halogen is rapidly discharged until equilibrium is established; this is disturbed by dilution, and more iodine is decolorised; in order to reach the point of stable equilibrium corresponding with the completion of the above equation, it is necessary to attain such a degree of dilution that the proportion of thiocarbamide does not exceed about 0·02 per cent.* Under the latter condition, as was shown some years ago by Emerson Reynolds and the author (Trans., 1903, **83**, 1), thiocarbamide in neutral, or preferably slightly acid, solution can be accurately estimated by means of a standard solution of iodine; beyond recognising the fact that one atom of iodine reacts with one molecule of thiocarbamide, removing hydrogen as hydriodic acid, the change was not further investigated.

Before entering into an explanation of the causes which bring about equilibrium during the progress of this interaction, it is necessary, for a clear understanding of the subject, to describe in detail the peculiar properties of formamidine disulphide and its salts, and more particularly the hydriodide.

Preparation and Properties of Formamidine Disulphide Hydriodide and Certain other Salts of the Base.

The compound $C_2S_2N_4H_6,2HI$ was first obtained by McGowan (Trans., 1886, **49**, 195) by the interaction of iodine and thiocarbamide in the presence of alcohol; more recently H. Marshall (*Proc. Roy. Soc. Edin.*, 1902, **24**, 233) prepared and examined it, having obtained it from the interaction of the two substances in presence of water; unfortunately, both these investigators were misled as regards the true nature of the compound formed, which they considered to be an additive compound, "dithiocarbamide di-iodide," $(CSN_2H_4)_2I_2$, the formation of hydriodic acid and the saline character of the substance having escaped their attention. When iodine and thiocarbamide are allowed to interact in the presence of a

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* The presence of potassium iodide in the iodine solution has a very marked influence on the equilibrium; in its absence, the stable point can be reached earlier, as described later on.

solvent capable of bringing about even a feeble degree of ionisation, a reaction ensues in accordance with the equation:

$$2CSN_2H_4 + I_2 \rightleftharpoons C_2S_2N_4H_6,2HI.$$

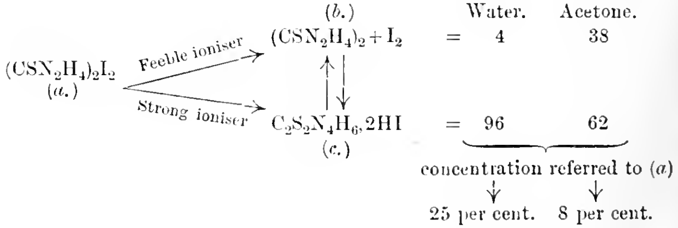
The amount of formamidine disulphide hydriodide produced is inversely proportional to the concentration of the products when equilibrium is established, and directly proportional to the ionising power of the solvent; for the latter reason water is by far the best medium for preparing the compound in its purest form.

A concentrated aqueous solution, prepared by gradually adding water to a mixture of powdered iodine and thiocarbamide in the above ratio until complete dissolution is effected, when allowed to evaporate, spontaneously deposits crystals of the hydriodide, chiefly in well-defined, flat, oblong, rectangular prisms, mixed with hexagonal and octagonal forms. The crystals, which are almost colourless, melt and decompose at 81°, yielding an orange-red liquid. When dissolved in a small quantity of water, some iodine is liberated, due to reversion; on dilution, a colourless solution is obtained, which is capable of decolorising a further small proportion of iodine; this, together with the fact that the percentage of iodine in the crystals has always been found to be from 2 to 3 per cent. lower than that required for the compound $C_2S_2N_4H_6,2HI$, proves that the crystals contain a small proportion of thiocarbamide in the free state, a natural consequence of the reversion of the hydriodide to iodine and thiocarbamide, as the concentration increases up to the point of crystallisation.

The crystals of the hydriodide separated from the solution, prepared as described, are quite insoluble in chloroform. When the solution is allowed to evaporate to dryness, the crystalline residue, although highly coloured, does not give up any free iodine to chloroform; the latter assumes a pale yellowish-brown colour, which changes to pale violet on heating, and reverts to the original colour when allowed to cool. This is due to the presence of a small quantity of a true additive compound of thiocarbamide and iodine which is formed when the solution is allowed to evaporate to dryness. This compound, which has the composition $(CSN_2H_4)_2I_2$, can be prepared readily by acting on finely powdered dry thiocarbamide with excess of iodine in benzene solution, and is obtained in this way as a pale buff-coloured, microcrystalline powder. It melts at 87° to a brownish-black liquid; unlike the hydriodide of formamidine disulphide, it is distinctly soluble in chloroform (approximately 0·6 per cent.), giving a yellowish-brown solution, and, as indicated by the colour changes mentioned above, undergoes dissociation on heating. When moistened with a drop of a solution of sodium hydrogen carbonate there is immediate brisk effervescence, as a result of the formation of hydriodic acid the moment the additive compound comes in contact with water; a separation of sulphur also occurs from the decomposition of the formamidine disulphide simultaneously produced. This additive compound, "dithiocarbamide di-iodide," can only exist in the dry state, or in solution in a non-ionising solvent, such as dry chloroform; when the aqueous solution is diluted to the point of producing a colourless liquid, the hydriodide, $C_2S_2N_4H_6,2HI$, alone is quantitatively formed, and the solution has no further decolorising effect on iodine.*

Since, as already mentioned, the formation of the hydriodide is favoured by the ionising power of the solvent, if methyl alcohol, ethyl alcohol, or acetone respectively are added to the colourless aqueous solution of the hydriodide, they cause immediate liberation of iodine by diminishing the ionisation, the amounts liberated being in the inverse order of their ionising power, the acetone in this case producing the most marked effect. These facts were noticed by Marshall (*loc. cit.*), who studied the dissociation of the compound in solution under the belief that he was dealing with the additive compound described above, but which, as now shown, could not possibly have been so.

The action of ionising solvents on the additive compound may be represented by the following scheme, with the actual results obtained with water and acetone introduced as a comparative illustration:



The numbers given represent the relative proportions of the products (*b*) and (*c*) generated by dissolving equal weights of (*a*) in the respective solvents, so as to produce approximately saturated solutions at the ordinary temperature. The free iodine of product (*b*) can only be estimated colorimetrically, as titration at once disturbs the equilibrium, and causes more of (*c*) to pass into (*b*); for this reason it was necessary to dilute the solution in acetone to a slight extent in order to obtain a fairly accurate result, on account of the large proportion of iodine liberated.

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* That is, for a reasonable limit of time, as the formamidine disulphide is slowly subject to indirect oxidation by iodine solution.

Formamidine disulphide hydriodide is capable of uniting with iodine to form a *periodide*, $C_2S_2N_4H_6,2HI,I_2$; this is a heavy, greenish-black liquid, dark brown by transmitted light; it is insoluble in cold water, and very sparingly soluble in chloroform. The following salts of formamidine disulphide have been prepared and examined for comparison with the hydriodide in connexion with the peculiar results to be presently described.

The hydrochloride, $C_2S_2N_4H_6,2HCl$, is conveniently prepared by adding sulphuryl chloride gradually to a cold solution of thiocarbamide in absolute alcohol, when it is precipitated almost quantitatively in colourless, microscopic needles, in accordance with the equation:

$$2CSN_2H_4 + SO_2Cl_2 = C_2S_2N_4H_6,2HCl + SO_2.$$

It melts and decomposes at 155°, and is very freely soluble in water.

The nitrate, $C_2S_2N_4H_6,2HNO_3$, melts and decomposes at 110°.

The *picrate*, $C_2S_2N_4H_6,2C_6H_3O_7N_3$, forms pale yellow, microscopic needles, or orange-coloured, flat, oblique, six-sided prisms. Both crystalline forms melt at 154°; this derivative may be conveniently used for the identification of the base when formed in very small quantity in a particular reaction.

The *platinichloride*, $C_2S_2N_4H_6,H_2PtCl_6$, decomposes without melting at 180°.

Aqueous solutions of all the salts examined decompose at 70—80°, with separation of sulphur; the decomposition is similar to that which is effected instantly on the addition of an alkali at the ordinary temperature, and is represented thus:

$$C_2S_2N_4H_6,2HX + 2NaOH = CSN_2H_4 + S + CN{\cdot}NH_2 + 2NaX + H_2O.$$

The base, when liberated from its salts either by alkali or by dissociation by heat, decomposes into thiocarbamide, sulphur, and cyanamide. This equation has been confirmed quantitatively as regards the proportion of thiocarbamide produced, and the above reaction has proved very useful in helping to elucidate the conditions of equilibrium which are found to exist in the interaction under investigation.

Nascent hydrogen in acid solution readily converts the base wholly into thiocarbamide, thus:

$$C_2S_2N_4H_6 + H_2 = 2CSN_2H_4.$$

The Behaviour of the Salts of Formamidine Disulphide towards the Alkali Iodides.

When potassium iodide is added to an aqueous solution of the hydriodide of the base there is immediate liberation of iodine, due to a diminution in the ionisation of the solution, and consequent reversion of a certain quantity of the hydriodide to thiocarbamide and free iodine; this effect was noticed by H. Marshall (*loc. cit.*) when studying the properties of the hydriodide, viewed in the light of an additive compound, $(CSN_2H_4)_2I_2$. The liberation of iodine increases with successive additions of the alkali iodide until a stable point is reached.

The extremely sensitive behaviour of the hydriodide is shown in the following experiments:

I. When a solution of the salt is diluted well beyond the point of stable equilibrium, the addition of a crystal of potassium iodide is followed by immediate liberation of iodine.

II. Solutions of the nitrate and chloride of the base, to which the theoretical amount of sodium acetate has been previously added (to eliminate as far as possible the formation of the hydriodide), give immediate liberation of iodine on addition of the alkali iodide.

III. The presence of excess of thiocarbamide in the solution does not prevent the liberation of iodine the moment a crystal of potassium iodide is added; the free iodine quickly disappears on shaking in this case.

A quantitative study of the interaction has revealed an interesting equilibrium which is capable of existing between the base and thiocarbamide under conditions where simultaneous reduction and oxidation may obtain, as shown in the following results.

Milligram-molecular equivalents of the three * salts of the base, namely, the nitrate, hydrochloride, and hydriodide, were separately dissolved in 25 c.c. of water, and 1 gram of potassium iodide was added; the amount of iodine liberated when determined colorimetrically was equal to only 0·5 c.c. of $N/10$-iodine solution. When the free iodine was removed by addition of sodium thiosulphate, equilibrium was at once disturbed, and more iodine was set free, and in order to reach the stable point, 10 c.c. of $N/10$-sodium thiosulphate were required, that is, an atomic proportion only of iodine was liberated when equilibrium was established. Sodium hydroxide solution was now added; there was instant precipitation of sulphur, proving the presence of unchanged formamidine disulphide in the

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* The concentration of the base is the same in each case, and the three different salts were experimented with in order to prove that the results are not affected by the other ions present.

solution; when the amount of the base was determined, by aid of the equation already given, it was found that half the quantity originally taken was still present in the solution. Equilibrium was therefore established when the base and thiocarbamide were exactly present in the proportions $C_2S_2N_4H_6 : 2CSN_2H_4$. This condition is, no doubt, brought about by the equal tendency of one to be converted into the other in the presence of water, and an agent such as iodine, capable of establishing a balanced interaction; this may be illustrated by the following scheme:

Formamidine disulphide.		Thiocarbamide
$C_2S_2N_4H_6 \longleftarrow$	H_2O	$\longrightarrow 2CSN_2H_4$
tending to form $2CSN_2H_4$.		tending to form the base.

The state of equilibrium containing the three components in the proportions:

$$C_2S_2N_4H_6,2HI : I_2 : 2CSN_2H_4,$$

can be realised by adding potassium iodide to a solution of the hydriodide of the base until iodine ceases to be liberated; a relatively large proportion of the alkali iodide is necessary, and probably for this reason the equilibrium in this case is not sensibly altered by moderate dilution.

It is evident from these results that the alkali iodide must play a very important part in retarding the point of stable equilibrium in the estimation of thiocarbamide by means of an ordinary standard solution of iodine. In view of some of the results just recorded, it seems not at all unlikely that the base may possess, under certain conditions, the power of setting free iodine from the alkali iodide; thus:

$$C_2S_2N_4H_6 + H_2O + 2KI = 2CSN_2H_4 + I_2 + K_2O.$$

Further investigation would be necessary to support this suggestion.

Conditions which Bring About an Equilibrium in the Interaction of Iodine and Thiocarbamide.

In the production of formamidine disulphide, in accordance with the interaction $2CSN_2H_4 + I_2 \rightleftharpoons C_2S_2N_4H_6,2HI$, three distinct final results can be realised, according to the following different conditions.

First, if the base is removed, as the very sparingly soluble dinitrate, as fast as it is produced, the interaction can be completed quantitatively in one direction, even with saturated solutions of the two components.

Secondly, when the equilibrium is disturbed by removing the free iodine,* dissociation of the hydriodide of the base continues until equivalent proportions of thiocarbamide and the hydriodide remain in solution, namely, $C_2S_2N_4H_6,2HI:2CSN_2H_4$.

Thirdly, under normal conditions, that is, in the absence of alkali iodide.

Final equilibrium is only established when the dilution is brought to a point corresponding with 0·04 per cent. of thiocarbamide in solution. If alkali iodide is present, as when ordinary *N*/10-iodine solution is used, a dilution twice as great is necessary.

This high degree of dilution which is required to reach the stable point is remarkable, bearing in mind that an almost saturated aqueous solution of the hydriodide of the base does not contain more than about 4 per cent. of thiocarbamide and iodine together in the free state.

The following few results are sufficient to show the enormous influence of alkali iodide in retarding the completion of the interaction, and also to illustrate how the change proceeds regularly with dilution, using ordinary *N*/10-iodine solution.

Thiocarbamide, per cent.								
1·0	equilibrium	established	when	29·0	per cent.	is converted	into the	base.
0·5	,,	,,	,,	38·6	,,	,,	,,	,,
0·25	,,	,,	,,	48·6	,,	,,	,,	,,
0·125	,,	,,	,,	58·3	,,	,,	,,	,,
0·0625	,,	,,	,,	68·1	,,	,,	,,	,,
0·01563	,,	,,	,,	100·0	,,	,,	,,	,,

As the dilution approaches the stable point, it is not easy to distinguish between the stage at which an equilibrium is just established and the point when iodine is present in excess. The details are given in the experimental part of the paper.

The production of formamidine disulphide by the action of iodine on thiocarbamide presents a further point of theoretical interest when compared with the production of the base by the action of direct oxidising agents on thiocarbamide. When any one of the following: potassium permanganate, hydrogen peroxide, potassium chlorate, sodium nitrite, or even ferric chloride is added to an aqueous solution of thiocarbamide containing a small quantity of nitric, sulphuric, or hydrochloric acid, the base is immediately formed, and its presence is easily demonstrated by (*a*) the precipitation of sulphur on addition of ammonium hydroxide, (*b*) the separation of the crystalline picrate on addition of a concentrated solution of picric acid.

When any one of these agents, with the exception of ferric

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* This will only occur at concentrations before the stable point is reached; beyond 0·04 per cent. of thiocarbamide, the hydriodide of the base is alone present in solution.

chloride, is added to a solution of thiocarbamide containing acetic acid, or any other equally feeble ioniser, or to a neutral solution, the base is not formed, as proved by the negative results obtained with the tests above mentioned.

The behaviour of nitrous acid towards thiocarbamide under these two different conditions has been carefully investigated, and the results which are recorded on p. 2184 have led to a new suggestion regarding the constitution of thiocarbamide. In the interaction of iodine and thiocarbamide, the base is formed just as readily under all three conditions, from which it may be inferred that the production of hydriodic acid the moment the interaction starts, determines the necessary configuration of the thiocarbamide molecule, suitable to the production of formamidine disulphide.

As water plays an all-important part in determining the interaction, further experiments are in progress in the hope of obtaining more information as regards the exact mechanism of the change.

The behaviour of certain substituted derivatives of thiocarbamide towards iodine is being investigated with the above object in view.

EXPERIMENTAL.

Preparation of Dithiocarbamide Di-iodide.

Powdered iodine was gradually added to finely pulverised thiocarbamide in presence of pure dry benzene, until after thorough trituration in a glass mortar, iodine remained in excess in benzene solution. The dark brown powder so obtained was digested with cold chloroform, and finally thoroughly extracted with that solvent until all traces of free iodine were removed.

A pale buff-coloured, microcrystalline powder was thus obtained, which melted at 87°. (Found, $I = 62{\cdot}45$. $(CSN_2H_4)_2I_2$ requires $I = 62{\cdot}56$ per cent.)

The compound is sparingly soluble in cold chloroform, giving a pale yellowish-brown solution (approximate solubility equal 0·7 per cent.), which becomes violet on heating, and regains its original colour when cold; the substance is therefore easily dissociated by heat. It is readily dissolved by water with immediate transformation into the hydriodide of formamidine disulphide, $C_2S_2N_4H_6,2HI$.

Analysis of Formamidine Disulphide Hydriodide.

Several preparations of this compound were made by direct action of water or a mixture of iodine and thiocarbamide in the required proportions, and by solution of the additive compound in the minimum amount of water. The finest crystals were obtained by slow, spontaneous evaporation at the ordinary temperature in flat, rectangular prisms mixed with well-defined, hexagonal and octagonal forms. The crystals melt at 81°, and after pressure between folds of bibulous paper, and, drying in a desiccator, are almost colourless. Analytical data of different specimens are as follows:

I. First crystals deposited:

0·2 gave, on distillation with ferric sulphate, 0·1194 I. I=59·7.

II. Second crystals from mother liquor:

0·2 gave 0·1181 I. I=59·05.

III. Third crystals from mother liquor from II:

0·2 gave 0·1172 I. I=58·6.

IV. Crystals obtained by dissolving $(CSN_2H_4)_2I_2$ in minimum amount of water at 15° and cooling solution to −4°:

0·2 gave 0·12065 I. I=60·32.

$C_2H_6N_4S_2,2HI$ requires I=62·56 per cent.

0·5 Gram of preparation IV dissolved in 250 c.c. of water and titrated with *N*/10-iodine, using starch as indicator, required 1 c.c.=1·52 per cent. of free thiocarbamide. These results show that the reversion to thiocarbamide and free iodine, which increases with the concentration, leads to the separation of crystals which are contaminated with thiocarbamide in proportion as the evaporation proceeds; for this reason it is not possible to obtain the hydriodide in a pure state from its solution.

The periodide, precipitated as a heavy, black liquid by adding a concentrated solution of iodine to a solution of the hydriodide, gave, without any further purification, the following results on analysis:

0·371, distilled with ferric sulphate, gave 0·2857 I. I=77·02.

$C_2H_6N_4S_2,2HI,I_2$ requires I=76·96 per cent.

This compound can be directly prepared by triturating molecular proportions of iodine and thiocarbamide under water, in which it is quite insoluble.

The *picrate* of formamidine disulphide is precipitated even from very dilute solutions of any of the salts in pale yellow, microscopic needles, which on remaining for some time in the liquid gradually change to orange-yellow, six-sided prisms, melting at 154°:

0·1096 gave 21·8 c.c. N_2 at 19° and 763 mm. N=23·08.

$C_2H_6N_4S_2,2C_6H_2O_7N_3$ requires N=23·02 per cent.

A monopicrate would require N=25·85 per cent.

The Platinichloride, $C_2S_2N_4H_6,H_2PtCl_6$.—A solution of platinic chloride was added to a cold concentrated solution of the hydrochloride of the base. An orange-yellow, crystalline compound was soon precipitated in minute, hexagonal prisms. It was washed with ice-cold water, in which it is almost insoluble:

0·2621 gave 0·0914 Pt. Pt = 34·87.
$C_2H_6N_4S_2,H_2PtCl_6$ requires Pt = 34·82 per cent.

Preparation of the Dinitrate of formamidine Disulphide.

The formation of this characteristic salt has been used as a rapid and trustworthy means of determining the amount of the base produced by the action of different oxidising agents on thiocarbamide. The details of its preparation with this object in view are as follows: 0·76 gram of thiocarbamide is a convenient weight to use. This is dissolved in 25 c.c. of water, 1·5 c.c. of nitric acid (D 1·42) are added, and the solution cooled in a freezing mixture to about 0°; the particular oxidising agent in moderately concentrated solution is gradually added, with constant stirring, to the thiocarbamide solution, until a drop of the liquid, brought in contact with a drop of dilute iodine solution, has no longer any decolorising effect on the latter. The microcrystalline precipitate of the dinitrate is quickly collected, washed with absolute alcohol, and then with ether, dried in the air, and weighed.

The theoretical yield of the dinitrate from 0·76 gram of thiocarbamide is 1·38 grams. The following amounts were obtained with the different agents mentioned; in the case of iodine the thiocarbamide was directly treated with the theoretical amount of the element dissolved in potassium iodide solution.

			Theoretical proportion.
I.	With iodine, yield of dinitrate	= 1·37 grams	= 99·34 per cent.
II.	,, $NaNO_2$, ,, ,,	= 1·28 ,,	= 92·75 ,,
III.	,, H_2O_2 ,, ,,	= 1·24 ,,	= 89·85 ,,
IV.	,, $KMnO_4$,, ,,	= 1·02 ,,	= 73·91 ,,

The dinitrate is very unstable when in a fine state of division, and decomposes spontaneously when dry after a very short time, in several instances violent decomposition took place within two hours from the time of its preparation:

0·2935 gave 0·49 $BaSO_4$. S = 22·95.
0·185 ,, 46·8 c.c. N_2 at 16·5° and 772 mm. N = 30·17.
$C_2H_6N_4S_2,2HNO_3$ requires S = 23·18 per cent. N = 30·43 per cent.

A *N*/100-solution decomposes with separation of sulphur at 71—72°; cyanamide and thiocarbamide are the other products.

0·276 Gram of the salt was decomposed in aqueous solution by heating for ten minutes at 80°; the sulphur was removed by filtration. The filtrate on titration with *N*/10-iodine (Reynolds and

Werner's method, Trans., 1903, **83**, 7) required 11·4 c.c.=0·08664 thiocarbamide. The equation:

$$C_2S_2N_4H_6 = CSN_2H_4 + S + CN_2H_2,$$

using the dinitrate (M.W.=276), requires 0·076 thiocarbamide. The amount found is 14 per cent. in excess of theoretical.

Decomposition of the Dinitrate by Sodium Hydroxide.

2·76 Grams of the salt were suspended in 100 c.c. of water; *N*-sodium hydroxide solution was gradually added, with constant stirring, until the liquid showed faint alkalinity, using phenolphthalein as indicator; 20·3 c.c. were required, whereas 20 c.c. are demanded by the equation:

$$C_2S_2N_4H_6,2HNO_3 + 2NaOH = CSN_2H_4 + S + CN_2H_2 + 2H_2O + 2NaNO_3.$$

The sulphur, after being collected, washed, and dried, weighed 0·225 gram, whereas theory requires 0·32 gram; the thiocarbamide was titrated in the filtrate, as before, 0·785 gram being found, whilst theory requires 0·76 gram, a result only slightly in excess of theory, whilst the amount of sulphur precipitated is only 70·31 per cent. of that required by the equation given.

In a similar experiment with the hydrochloride, $C_2S_2N_4H_6,2HCl$:

2·23 gave 0·235 S and 0·788 CSN_2H_4. Theory=0·32 S and 0·76 CSN_2H_4.

No alkaline sulphide is formed, from which it appears likely that a portion of the sulphur is contained in a product of secondary decomposition, the nature of which has not yet been proved. Cyanamide was qualitatively determined by extracting the liquid with ether, which on evaporation left a residue which readily gave the characteristic bright yellow precipitate of silver cyanamide on addition of ammonio-silver nitrate. The verification of the yield of thiocarbamide produced in this decomposition was the main point under consideration in connexion with the present investigation.

Solubility of the Dinitrate.—This was determined by estimation of the thiocarbamide produced on decomposition by alkali.

In water containing 5 per cent. of nitric acid=0·03 per cent.
In water alone=2·08 „ „

Action of Nascent Hydrogen on Formamidine Disulphide.

0·37 Gram of the dinitrate was dissolved in 100 c.c. of water, and left in contact with excess of zinc turnings and dilute sulphuric acid for one hour, after which the solution was titrated with *N*/10-iodine, of which 26·4 c.c. were required=0·2006 CSN_2H_4.

The equation $C_2S_2N_4H_6 + H_2 = 2CSN_2H_4$ requires 0·2036. The base is therefore quantitatively reduced to thiocarbamide in a very short time, a reaction which tends to confirm the constitution assigned to the compound.

Results obtained on the Titration of Thiocarbamide with N/10-Iodine in Neutral Solution at Different Concentrations.

When iodine solution is added to a neutral solution of thiocarbamide containing some starch as indicator, a lilac colour passing to deep violet is produced before the well-known pure blue colour is obtained, indicating iodine in excess. In the following titrations the lilac to violet colour was taken as the point indicating equilibrium, and the same volume (50 c.c.) of solution was used in each experiment.

	Thiocarbamide.	*N*/10-Iodine required.	Thiocarbamide converted into formamidine disulphide.
1.	1·0 per cent.	19·2 c.c.	29·0 per cent.
2.	0·5 ,,	12·7 ,,	38·6 ,,
3.	0·25 ,,	8·0 ,,	48·6 ,,
4.	0·125 ,,	4·8 ,,	58·3 ,,
5.	0·0625 ,,	2·8 ,,	68·1 ,,
6.	0·03125 ,,	1·6 ,,	77·8 ,,
7.	0·015625 ,,	1·05 ,,	100·0 ,,

When the concentration of thiocarbamide falls below 0·02 per cent. it is practically impossible, using *N*/10-iodine, to distinguish an intermediate colour reaction before the pure blue of the starch iodide is produced.

This number represents the maximum limit of concentration which can be used for the accurate estimation of thiocarbamide by means of *N*/10-iodine solution.

Titration of Thiocarbamide by N/10-Iodine in Presence of Sodium Acetate.

In making the following titrations, the theoretical amount of sodium acetate required to react with the hydriodic acid was previously added to the thiocarbamide solutions.

		Thiocarbamide present.	*N*/10-Iodine required.	Thiocarbamide converted into the base.
1.	50 c.c.	1·0 per cent.	31·8 c.c.	48·33 per cent.
2.	50 ,,	0·304 ,,	11·1 ,,	55·5 ,,
3.	50 ,,	0·10 ,,	3·8 ,,	57·76 ,,

These results are sufficient to show that whilst the presence of sodium acetate enables the interaction to proceed further in the more concentrated solution, even the partial neutralisation of the hydriodic acid which must occur in this case does not materially increase the amount of the formamidine disulphide produced in the dilute solutions. This is probably due to the equilibrium which exists between the base and thiocarbamide already mentioned.

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CCXXVIII.—*The Action of Nitrous Acid on Thiocarbamide and on Formamidine Disulphide. A New Structural Formula for Thiocarbamide.*

By Emil Alphonse Werner.

Storch (*Monatsh.*, 1890, **11**, 452) has shown that when nitrous acid, in common with several other oxidising agents, is added to an acid solution of thiocarbamide, the feeble base

$$HN\colon C(NH_2)\cdot S\cdot S\cdot (NH_2)\cdot C\colon NH$$

is produced, for which Fichter and Wenk (*Ber.*, 1912, **45**, 1373) have recently proposed the name formamidine disulphide. The present author (this vol., p. 2169) has pointed out that Storch's base is only formed by the action of oxidising agents on thiocarbamide when a strong acid ioniser is present. The base can be readily detected in solution, even when present in very small quantity, by (*a*) the immediate precipitation of sulphur on addition of ammonium hydroxide, and (*b*) the separation of the crystalline picrate (m. p. 153°) on addition of picric acid solution. When nitrous acid, or an alkali nitrite, was added to a solution of thiocarbamide containing sulphuric, nitric, or any other strong acid, an evanescent, red coloration was produced, whilst gas, consisting chiefly of nitric oxide, was rapidly evolved, and on applying the above tests the presence of formamidine disulphide was at once revealed. When the same experiment was made with a solution of thiocarbamide containing acetic acid, or any other equally feeble acid ioniser, such as nitrous acid itself, only a faint, yellow coloration was produced, gas was evolved which consisted chiefly of nitrogen, and on the application of the tests no formamidine disulphide could be detected; the addition of ferric chloride produced an intense blood-red colour due to thiocyanic acid formed as a result of the interaction; no such colour reaction was given with ferric chloride in the former experiment, until an excess of nitrous acid had been added; this is explained later.

Claus (*Annalen*, 1878, **179**, 129) examined the action of ethyl nitrite on an alcoholic solution of thiocarbamide, and considered the main change to consist in the reversion of the latter to ammonium thiocyanate; later A. E. Dixon (Trans., 1892, **61**, 526), as a side-issue of an investigation on the constitution of certain complex derivatives of thiocarbamide, was led to repeat Claus' experiments, and showed that free thiocyanic acid is produced in the reaction, whilst not a trace of ammonia could be detected. The following equation has been given by Dixon as representing the chief result of the decomposition by nitrous acid:

$$CSN_2H_4 + HNO_2 = HSCN + N_2 + 2H_2O,$$

and this has been confirmed in the main as the result of a quantitative study of the change.

It is obvious from the facts just recorded that the interaction of nitrous acid and thiocarbamide proceeds on two different lines according as a strong or a weak acid ioniser is present in the solution; the following results also show that the reaction, so far as the production of thiocyanic acid * is concerned, is divisible into two distinct stages when a strong acid is present, but is completed in a single stage in the presence of a weak acid.

When the theoretical amount of pure sodium nitrite was added gradually to a solution of thiocarbamide containing about 5 per cent. of nitric acid, the very sparingly soluble formamidine disulphide dinitrate, $C_2S_2N_4H_6,2HNO_3$, was obtained, in accordance with the equation:

$$2CSN_2H_4 + 2HNO_2 = C_2S_2N_4H_6 + 2NO + 2H_2O,$$

in amount equal to 92·39 per cent. of the theoretical, and by using a slight excess of the alkali nitrite the yield was increased to 93·75 per cent., which was the maximum obtainable.

In order to obtain a clear idea regarding the progress of the interaction under the different conditions mentioned, quantitative experiments were carried out in a Lunge's nitrometer, the full details of which are described in the experimental part.

A. *Examination of the* 1*st Stage.*—A known weight of thiocarbamide, together with the theoretical amount of pure sodium nitrite dissolved in a small quantity of water, was introduced into the nitrometer, and a sufficient amount of dilute sulphuric acid added. Gas was evolved with great rapidity, the liquid which at first assumed a red colour quickly changed to pale yellow, and the reaction was complete in a few minutes. The total volume of gas, which was in perfect agreement with the above equation, was found always to contain about 12 per cent. of nitrogen.

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* Thiocyanic acid is slowly further oxidised by nitrous acid, with production of pure nitric oxide.

This is due to interaction of nitrous acid and formamidine disulphide, which accompanies the primary change, and explains at once the slight deficiency in the yield of the base, noticed in the previous experiment.

B. *Examination of the 2nd Stage.*—Experiment A was repeated, and after the evolved gas had been expelled from the nitrometer, a second theoretical amount of the alkali nitrite dissolved in a small quantity of water was introduced. A small quantity of gas was rapidly evolved; this was followed by a short interval of quiescence, after which gas was set free with increasing rapidity, whilst the liquid became deep red in colour. The reaction was completed in a few minutes. The total volume of gas was almost identical with that evolved in the first stage; it contained nearly 16 per cent. of nitric oxide; the remainder was nitrogen, and the residual liquid was rich in thiocyanic acid.

It is obvious from the results of experiment A that the liquid at the end of the first stage must contain a small quantity of unchanged thiocarbamide, to which is due the sudden evolution of a small amount of gas, preceding the quiescent phase when stage two properly speaking really starts, and which also accounts for portion of the nitric oxide found.

The decomposition in the second stage may be provisionally explained by the following equations:

$$NH_2\cdot(NH\colon)C\cdot S_2\cdot C(\colon NH)\cdot NH_2 + 2HONO = HO\cdot(NH\colon)C\cdot S_2\cdot C(\colon NH)\cdot OH + 2H_2O + 2N_2.$$

$$HO\cdot(NH\colon)C\cdot S_2\cdot C(\colon NH)\cdot OH = 2HSCN + H_2O + O.$$

No oxygen could be detected in the gaseous product, as it was used up in oxidising some of the thiocyanic acid, the amount of which in the residual liquid was found to be only 83·56 per cent. of that required by the above equation. The oxidation of thiocyanic acid takes place as follows: $HSCN + 3O = SO_3 + HCN$; one atomic proportion of oxygen would therefore be capable of oxidising one-sixth of the total quantity of thiocyanic acid produced, that is, 16·66 per cent., the difference between the theoretical and the amount actually found, namely, 100—83·56 = 16·44, is in close agreement with this result.

When nitrous acid and thiocarbamide or formamidine disulphide were allowed to interact in the presence of dilute acetic or nitric acid, a small quantity of sulphuric acid was always found in the final product; in one experiment carried out in presence of dilute nitric acid, the sulphuric acid formed was estimated, and was found to correspond with the deficiency in the thiocyanic acid (see Expt. III).

C. *Examination of the Interaction in a Single Operation in*

Presence of Dilute Sulphuric Acid.—A solution containing two molecular proportions of alkali nitrite and one of thiocarbamide was directly treated with dilute sulphuric acid in the nitrometer. The evolution of gas was very rapid at the start, and whilst no quiescent stage could be detected, there was very perceptible diminution in the violence of the reaction when about half the final volume of gas had been evolved. The proportion of nitric oxide amounted to 58·5 per cent.; the remainder was nitrogen; the equation:

$$2CSN_2H_4 + 4HNO_2 = 2HSCN + 2N_2 + 2NO + 5H_2O + (O)$$

requires equal volumes of the two gases. Since in all these interactions the departure from the theoretical, as regards the composition of the gas evolved, is always NO for N_2, or vice versa, the final volume of gas has been found in each case to agree very closely with that required by the equation.

D. *Examination of Interaction in Presence of Acetic Acid, one stage only.*—Equal molecular proportions of thiocarbamide and sodium nitrite, dissolved in a small quantity of water, were treated with sufficient dilute acetic acid in the nitrometer. A slight brownish-red colour is at first developed, which quickly changed to pale yellow, gas was freely evolved, and the reaction was completed after a few minutes. The total volume of gas set free was in perfect agreement with the equation:

$$CSN_2H_4 + HNO_2 = HSCN + N_2 + 2H_2O;$$

it was found, however, to contain 8·6 per cent. of its volume of nitric oxide, whilst the amount of thiocyanic acid present in the residual solution was 85·3 per cent. of that required by the equation. No formamidine disulphide could be detected as a product of the change; the nitric oxide must therefore have been produced as a by-product of the oxidation of a portion of the thiocyanic acid, and as some sulphuric acid was found in the solution this is confirmed.

When the interactions just described are carried out in very dilute solutions, the composition of the evolved gas is not altered, proving that the secondary reactions are not influenced by dilution.

The main results obtained may be briefly summarised as follows, leaving aside the secondary changes:

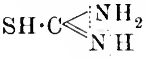
(i) When nitrous acid and thiocarbamide interact in aqueous solution in the presence of a weak acid, thiocyanic acid is directly produced with evolution of nitrogen, and the change takes place between equal molecular proportions of the two compounds.

(ii) When nitrous acid and thiocarbamide interect in aqueous solution in the presence of a strong acid, formamidine disulphide is produced with evolution of nitric oxide, and is then decomposed with formation of thiocyanic acid, and evolution of nitrogen. Two molecular proportions of nitrous acid to one of thiocarbamide are required to complete the change.

(iii) The respective interactions are independent of the concentration.

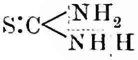
(iv) Nitrites may be rapidly and accurately estimated by means of thiocarbamide.

The reactions and properties of formamidine disulphide are in agreement with the constitutional formula originally proposed by Storch (*loc. cit.*), namely, $NH_2\cdot(NH{:})C\cdot S_2\cdot C({:}NH)\cdot NH_2$, and its production from thiocarbamide has been generally accepted as strong evidence in support of the unsymmetrical formula $NH_2\cdot C({:}NH)\cdot SH$ for the latter. Storch was led to conclude from his work that thiocarbamide in acid solution, at all events, has this constitution. It is evident from the results recorded in the present paper, and also in that on "The Interaction of Iodine and Thiocarbamide" (this vol., p. 2166), that this view of the constitution of the substance is not alone sufficient to explain the different facts observed. There can certainly be little, if any, objection to the proposition that the production of thiocyanic acid is in better agreement with the unsymmetrical than with the symmetrical formula of thiocarbamide, namely,



$$\mathrm{SH\cdot C}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH}\end{matrix}$$

(I.)



$$\mathrm{S{:}C}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH\,H}\end{matrix}$$

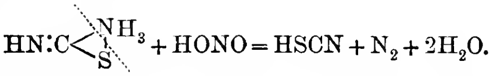
(II.)

even if the change of H·NCS into H·SCN as derived from formula (II) is admitted. To support the unsymmetrical formula it might also be argued that since formamidine disulphide is only stable in presence of a strong acid, it may be produced as an intermediate product when nitrous acid reacts with thiocarbamide in the presence of a weak acid, but having under such conditions only an ephemeral existence it is immediately decomposed into thiocyanic acid with evolution of nitrogen. This, however, is contrary to the observed facts, for a much larger proportion of nitric oxide would be produced if this took place.

If the unsymmetrical formula, therefore, is accepted, and it is the more likely, it is evident that the presence of a strong acid, in bringing about a condition favourable to the production of formamidine disulphide, must induce an alteration in the structure of the thiocarbamide molecule which is not produced by the presence of a weak acid, and is different from that pre-existent in the ordinary neutral solution of the substance.

The following theory of the constitution of thiocarbamide does not appear to have been hitherto suggested, and seems to have a serious claim to consideration, since it offers an important clue to the explanation of the particular phenomena under discussion.

In the structural formula $HN{:}C{<}^{NH_2}_{SH}$ a mutual attraction must exist between the respective positive and negative NH_2- and SH-groups, resulting in the assumption of a configuration represented by the formula $HN{:}C{<}^{NH_3}_{S}$, bearing in mind that thiocarbamide is only capable of forming salts with the stronger acids, resembling in this respect the amino-acids and compounds of like constitution. A configuration such as this would not be disturbed by the presence of a feeble acid in solution, and hence would directly yield thiocyanic acid and nitrogen when attacked by nitrous acid, thus:

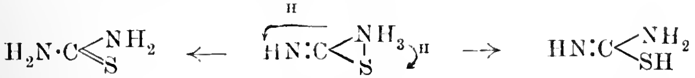


$$HN{:}C{<}^{NH_3}_{S} + HONO = HSCN + N_2 + 2H_2O.$$

The addition of a strong acid, on the other hand, would at once destroy the "ammonia constitution," and by producing a salt of the structure $NH{:}C{<}^{NH_2,HX}_{SH}$ would effect the necessary alteration in the constitution of the thiocarbamide required for the production of formamidine disulphide. The mechanism of the interaction of iodine and thiocarbamide can also be satisfactorily explained by the aid of this new formula (see p. 2175).

The structure of thiocarbamide which is now proposed, whilst it explains the phenomena under notice in a simple manner, has several other claims to consideration which must be left over for discussion in a future communication; attention, however, may be drawn to the following points, which have a direct bearing on the present investigation.

If this constitutional formula represents the structure of thiocarbamide under normal conditions, that is, in a neutral solution or even in the presence of a weak acid, it explains how the compound can give rise to products derived either from the symmetrical or unsymmetrical structure already recognised, according as the conditions are altered, thus:



$$H_2N{\cdot}C{\lessgtr}^{NH_2}_{S} \leftarrow HN{:}C{<}^{NH_3}_{S} \rightarrow HN{:}C{<}^{NH_2}_{SH}$$

(b.) Symmetrical. (a.) Normal structure. (c.) Unsymmetrical.

If (*a*) represents the normal structure, the migration of a hydrogen atom in either of the directions shown will at once give rise to structure (*c*) or (*b*) as the case may be, whilst the change from (*a*) to (*c*) is apparently determined by a strong acid or other reagent having a similar influence; the change from (*a*) to (*b*) (if such does occur) must require some other condition.

This formula also shows a much closer structural relationship between thiocarbamide and ammonium thiocyanate, and while it suggests that the transformation of the latter into the isomeric compound is brought about by the migration of a single atom of hydrogen, instead of two, as required by the other formulæ, it also gives a hint of the possible mechanism of the isomeric transformation being as follows: ammonium thiocyanate on heating dissociates partly into ammonia and thiocyanic acid, the latter changes to *iso*thiocyanic acid, which then re-unites with ammonia to produce thiocarbamide, from which it follows that the amount of the latter formed is in a great measure dependent on the extent of the dissociation of ammonium thiocyanate at the temperature of 170—180°, beyond which the thiocarbamide commences to decompose.

EXPERIMENTAL.

Action of Nitrous Acid on Thiocarbamide in Presence of Nitric Acid.

Expt. I.—0·76 Gram of pure thiocarbamide was dissolved in 40 c.c. of water, 2 c.c. of nitric acid (D 1·42) were added, and 0·69 gram of sodium nitrite * dissolved in 20 c.c. of water was added gradually with constant stirring while the liquid was cooled to about 0°. Formamidine disulphide dinitrate, $C_2S_2N_4H_6,2HNO_3$, was precipitated as a white, microcrystalline powder, which was collected, washed with absolute alcohol and then with ether, and dried in the air. The theoretical yield of the dinitrate, formed from the above weight of thiocarbamide in accordance with the equation:

$$2CSN_2H_4 + 2HNO_2 = C_2S_2N_4H_6 + 2NO + 2H_2O,$$

should be 1·38 grams, whilst the weight obtained was 1·275 grams or 92·39 per cent. of the theoretical.

Expt. II.—In this case the operation was carried out as before, but the alkali nitrite was added in slight excess, that is, until a drop of the solution just ceased to decolorise a drop of dilute iodine solution, which proved the absence of any unchanged thiocarbamide.

Weight of dinitrate obtained = 1·29 grams = 93·75 per cent. of the theoretical.

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* The specimen of sodium nitrite used in all the experiments contained 95·4 per cent. of $NaNO_2$, and a proportionate weight corresponding with the theoretical required was used in each case.

Expt. III.—1·52 Grams of thiocarbamide were dissolved in 150 c.c. of water containing 3 c.c. of nitric acid, and a 6 per cent. solution of sodium nitrite was gradually added with constant stirring until a drop of the solution ceased to give a precipitation of sulphur on addition of ammonium hydroxide solution, proving that all the formamidine disulphide was decomposed. At first there was evolution of brown fumes (due to the nitric oxide set free), but when slightly more than half the required amount of nitrite had been added, the brown fumes ceased, whilst gas (nitrogen) continued to be evolved to the end. The residual solution was made up to 300 c.c. by addition of distilled water:

41·5 c.c. were required for complete precipitation of 25 c.c. of $N/10$-$AgNO_3$. HSCN = 0·1475. Hence, total HSCN = 1·066 or 90·3 per cent. of the theoretical.

Theory requires 1·18 grams for the complete conversion of thiocarbamide into thiocyanic acid in accordance with the equation:

$$2CSN_2H_4 + 2HNO_2 = 2HSCN + 2N_2 + 4H_2O.$$

Formamidine disulphide was produced, and then decomposed by further addition of nitrous acid:

100 c.c. of the solution gave 0·1538 $BaSO_4$. Total = 0·4614. Hence HSCN = 0·116.

1·066 + 0·116 = 1·182 HSCN. Theory requires 1 18.

Expt. IV.—The last experiment was repeated, with the difference that the theoretical amount of sodium nitrite, namely, 2·76 grams, was added, and the solution diluted to 300 c.c.:

47·85 c.c. were required for complete precipitation of 25 c.c. of $N/10$-$AgNO_3$. Total, HSCN = 0·0986, or 83·56 per cent. of the theoretical (1·18).

The solution was found to contain a small quantity of unchanged thiocarbamide. The sulphuric acid formed was not estimated.

Action of Nitrous Acid on Thiocarbamide in the Presence of Acetic Acid.

Expt. V.—1·52 Grams of thiocarbamide were dissolved in 150 c.c. of water containing 5 c.c. of acetic acid, and 1·38 grams of sodium nitrite (molecular proportions) dissolved in 25 c.c. of water were added gradually as before. Gas was evolved, with slight accompaniment of brown fumes; the solution when tested immediately after the first addition of alkali nitrite gave a deep red colour with ferric chloride, but no precipitate of sulphur was produced on addition of ammonium hydroxide. The solution was diluted to 300 c.c.:

47·9 c.c. were required for precipitation of 25 c.c. of $N/10$-$AgNO_3$.
Total HSCN = 83·47 per cent. of theoretical.

The solution contained a small quantity of unchanged thiocarbamide. Sulphuric acid was formed, but was not estimated.

The last two experiments prove that when the theoretical amount of nitrous acid is added all the thiocarbamide is not decomposed, on account of the secondary reaction, namely, oxidation of thiocyanic acid, which accompanies the primary change.

Determination of the Volume and Composition of the Evolved Gases.

Expt. VI.—0·076 Gram of thiocarbamide and 0·069 gram of sodium nitrite dissolved in 2 c.c. of water were introduced into the nitrometer over mercury, and 1 c.c. of dilute sulphuric acid (1:7) was added. Gas was evolved with great rapidity, and the reaction was completed in a few moments. Heat was developed, and after twenty minutes the volume of gas was 24·3 c.c. at 18·5° and 764 mm., or 22·36 c.c. at 0° and 760 mm.

The equation:

$$2CSN_2H_4 + 2HNO_2 = C_2S_2N_4H_6 + 2NO + 2H_2O$$

requires 22·4 c.c. at 0° and 760 mm.

Ten c.c. of a freshly prepared saturated solution of ferrous sulphate were now introduced into the nitrometer.

Volume of residual gas = 3·1 c.c. The composition was therefore NO = 21·2 = 87·24 per cent., N = 3·1 = 12·76 per cent.

The residual gas was quite free from carbon dioxide, and had the properties of nitrogen. The presence of this gas is the result of the secondary reaction between nitrous acid and formamidine disulphide.

Expt. VII.—The last experiment was repeated, and the evolved gas having been expelled from the nitrometer, 0·069 gram of sodium nitrite dissolved in 1 c.c. of water was introduced. A small quantity of gas was immediately evolved, and after a few moments the evolution of gas continued with increasing rapidity, and the reaction was completed in a few minutes.

Volume = 23·8 c.c. at 18·5° and 764 mm., or 21·86 c.c. at 0° and 760 mm. After treatment with $FeSO_4$, volume = 20 c.c. The composition was therefore NO = 3·8 = 15·97 per cent., N = 20·0 = 84·03 per cent.

The nitric oxide is partly due to the presence of thiocarbamide which had escaped conversion into formamidine disulphide as a result of the secondary reaction which occurs in the first stage.

The interaction of nitrous acid and formamidine disulphide cannot be explained without admitting the production of oxygen, thus:

$$C_2S_2N_4H_6 + 2HNO_2 = 2HSCN + 2N_2 + 3H_2O + O.$$

This gas could not be present with nitric oxide, and the results show that the oxygen must oxidise some of the thiocyanic acid produced with evolution of nitric oxide, since the latter was in slight excess of the theoretical, whilst the nitrogen was correspondingly too low (see also Expt. XI.), thus:

1st stage	NO = 87·24	N = 12·76
2nd ,, ...	NO = 15·97	N = 84·03
	103·21	96·79

Expt. VIII.—0·076 Gram of thiocarbamide and 0·138 gram of sodium nitrite (that is, two molecular proportions of nitrous acid to one of thiocarbamide) were dissolved in 2 c.c. of water, and 1 c.c. of dilute sulphuric acid was added.

Volume of gas obtained = 49·4 c.c. at 19° and 757 mm., or 45·01 c.c. at 0° and 760 mm. After treatment with $FeSO_4$, volume = 21·5 c.c. The composition was therefore NO = 27·9 = 56·47 per cent., N = 21·5 = 43·53 per cent.

Thus, when the interaction was carried out in a single operation, the proportion of nitric oxide evolved was slightly greater than when the decomposition was completed in two stages. The residual solution contained some formamidine disulphide; the higher proportion of nitric oxide was due to the complete conversion of the thiocarbamide into the base in accordance with the first stage reaction.

Expt. IX.—0·076 Gram of thiocarbamide and 0·069 gram of sodium nitrite (molecular proportion) were dissolved in 2 c.c. of water and 1 c.c. of acetic acid added.

Gas obtained = 24·4 c.c. at 20° and 764 mm., or 22·33 c.c. at 0° and 760 mm.

Theory requires 22·4 c.c. at 0° and 760 mm. in accordance with the equation:

$$CSN_2H_4 + HNO_2 = HSCN + N_2 + 2H_2O.$$

After treatment with $FeSO_4$, volume = 22·3 c.c. at 20° and 764 mm. The composition was therefore NO = 2·1 = 8·61 per cent., N = 22·3 = 91·39 per cent.

The nitric oxide was present as a result of the oxidation of portion of the thiocyanic acid formed, and some unchanged thiocarbamide was found in the residual solution obtained in a repetition of this experiment.

The following experiment proves that the proportion of nitric oxide is not materially altered by dilution; the secondary reaction evidently proceeds just the same.

Expt. X.—0·076 Gram of thiocarbamide and 0·069 gram of sodium nitrite were dissolved in 16 c.c. of water* (a 0·5 per cent. solution of the two substances), and 1 c.c. of acetic acid was added.

Gas was very slowly evolved, as compared with the other experiments, fifty minutes being required to complete the interaction.

Gas obtained = 22·9 c.c. at 18° and 764 mm., or 21·16 c.c. at 0° and 760 mm. After treatment with $FeSO_4$, volume = 20·9 c.c. The composition was therefore NO = 2·0 = 8·73 per cent., N = 20·9 = 91·27 per cent., which is in close agreement with the last experiment; the smaller volume of gas evolved is due to the solvent action of the comparatively large quantity of water which was present.

Expt. XI. Direct Decomposition of Formamidine Dinitrate by Alkali Nitrite.—0·276 Gram of formamidine dinitrate was mixed with 1 c.c. of water in the cup of the nitrometer, and drawn into the tube; an additional c.c. of water was used to wash in the last traces of the salt; 0·138 gram of sodium nitrite dissolved in 2 c.c. of water was then introduced. Gas was immediately evolved, and the reaction was completed in a few minutes.

Gas obtained = 46·4 c.c. at 19° and 756 mm., or 42·22 c.c. at 0° and 760 mm. After treatment with $FeSO_4$, volume = 40. The composition was therefore NO = 6·4 = 13·79 per cent., N = 40·0 = 86·21 per cent.

The nitric oxide in this case was entirely a by-product of the oxidation of portion of the thiocyanic acid.

The Estimation of Nitrites by means of the Interaction with Thiocarbamide.

The results obtained in all the foregoing experiments have shown that the decomposition of thiocarbamide is incomplete when the theoretical amount of nitrous acid is used, on account of the secondary reaction which takes place. On the other hand, when molecular proportions of the two substances interact either in the presence of dilute sulphuric or acetic acid, the total volume of gas evolved is in perfect agreement with the respective equations which represent the change in each case.

For example, in Expt. VI, in presence of dilute sulphuric acid, the corrected volume of gas obtained was 22·36 c.c., and in Expt. IX., in presence of acetic acid, the corrected volume of gas obtained was 22·33 c.c.

Theory requires in each case 22·4 c.c. at 0° and 760 mm. The actual composition of the gas evolved is of no importance so far as

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* The water was previously boiled and quickly cooled.

the estimation of the nitrite is concerned, since nitric oxide takes the place of nitrogen, or vice versa, as the case may be. In order to test the method, a sample of sodium nitrite was carefully estimated by the well-known method, using ordinary carbamide, and after absorption of the carbon dioxide by means of sodium hydroxide, the following results were obtained:

0·069 gave 23·5 c.c. N_2 (moist) at 18° and 752 mm., or 21·37 c.c. N_2 (dry) at 0° and 760 mm.

Theory requires 22·4 c.c. $NaNO_2 = 95·4$ per cent.

Expt. A.—0·069 gram of sodium nitrite and 0·1 gram of thiocarbamide were dissolved in 2 c.c. of water, and having been introduced into the nitrometer, 1 c.c. of dilute sulphuric acid (1:7) was added.

Gas evolved = 23·7 c.c. at 18° and 752 mm., or 21·55 c.c. (dry) at 0° and 760 mm.

Expt. B.—An exact repetition of *A*, 1 c.c. of acetic acid being used instead of sulphuric acid.

Gas evolved = 23·7 c.c. at 18° and 752 mm., or 21·55 c.c. (dry) at 0° and 760 mm.

$$NaNO_2 = \frac{21·55}{22·44} = 96·21 \text{ per cent.}$$

The result, which is 0·81 per cent. higher than that obtained by using ordinary carbamide, is very probably the more correct, as the gas has merely to be read off directly, and no subsequent manipulation is required. Further experiments are in progress to test the method against other processes.

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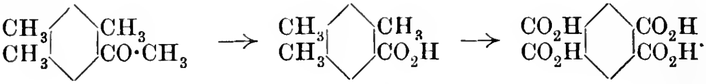
CCXXIX.—*The Preparation of Durylic and Pyromellitic Acids.*

By William Hobson Mills.

The method usually described for the preparation of pyromellitic acid is that of distilling mellitic acid with sulphuric acid (Baeyer, *Annalen Suppl.*, 1870, 7, 37; Silberrad, Trans., 1906, **89**, 1795). Since, however, mellitic acid is still an exceedingly costly substance to obtain through the usual commercial channels, a description of the method which was employed for the preparation of the pyromellitic acid necessary for the experiments recorded in the following communication may be of service. Acetyl-ψ-cumene, a substance which can easily be obtained from ψ-cumene in any quantity by the Friedel-Crafts reaction, served as the starting point of the process, which consisted in the conversion of acetyl-ψ-cumene by means of sodium hypobromite into durylic acid, and the subsequent oxidation of the latter to pyromellitic acid with potassium permanganate. Under the conditions specified, both reactions proceed very smoothly:



Experimental.

Durylic Acid.

Forty-five grams of acetyl-ψ-cumene are added to a solution of sodium hypobromite prepared from 67 c.c. of bromine and 930 c.c. of 3*N*-sodium hydroxide solution. The mixture is maintained at 68—70°, and stirred mechanically until bromine ceases to be liberated on acidification of a few drops of the liquid with acetic acid. This requires about one and a-quarter to one and a-half hours. The alkaline liquid is then separated from the mixture of bromoform and carbon tetrabromide produced, and sulphur dioxide is led into it until bromine is no longer set free on acidification with mineral acid. On the addition of hydrochloric acid to the hot solution, durylic acid is obtained as a snow-white precipitate. The yield of crude acid is about 90 per cent. of the theoretical; the melting point is, however, about 7° too low. The acid is best purified by taking advantage of the sparing solubility of its sodium salt in the presence of excess of sodium hydroxide. One hundred grams of the acid are dissolved in 300 c.c. of warm 3*N*-sodium hydroxide solution, and 150 c.c. of 20 per cent. sodium hydroxide solution are added. The liquid rapidly sets to a mass of soft, lustrous plates of the *sodium* salt. This salt is readily soluble in cold water or alcohol, but can be crystallised from hot acetone; the crystals contain two molecules of water of crystallisation:

0·4313 lost, at 150°, 0·0706, and gave 0·1394 Na_2SO_4. $H_2O = 16·4$; $Na = 10·43$.

$C_{10}H_{11}O_2Na,2H_2O$ requires $H_2O = 16·2$; $Na = 10·36$ per cent.

After collection, the sodium salt is dissolved in a considerable volume of hot water, and the acid precipitated with hydrochloric acid. In this manner 80 per cent of the acid taken can be obtained melting at 148—149°, and a further quantity can be isolated by a repetition of the process on the acid obtained by acidifying the mother liquor.

Pyromellitic Acid.

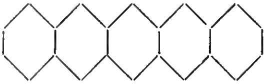
To a solution of 50 grams of durylic acid in 240 c.c. of 1·5*N*-potassium hydroxide, 1940 c.c. of a 5 per cent. solution of potassium permanganate (the calculated quantity for the oxidation of one methyl group) are added, in gradually increasing instalments, as each previous portion becomes decolorised, the temperature being kept at 70°. The temperature is then raised to 90°, and a second quantity of 1940 c.c. of the permanganate solution is added in three instalments, about one hour being required for the reduction of each. The third quantity (1940 c.c.) of the permanganate solution is then added all at once, and becomes decolorised after less than twelve hours' gentle boiling. Finally, the mixture is boiled for twenty-four hours with a further quantity of 800 c.c. of the permanganate solution, a considerable proportion of which should remain unreduced at the end of this period. Alcohol is added to remove the excess of permanganate, and the filtrate from the manganese dioxide is concentrated to small bulk, rendered faintly acid with acetic acid, and, while still hot, mixed with a boiling solution of 225 grams of crystallised barium chloride in 1200 c.c. of water. The insoluble barium pyromellitate, $C_{10}H_2O_8,2H_2O$, which is precipitated, is collected, washed, and dried, and then dissolved in ten parts of boiling 3*N*-hydrochloric acid. The calculated quantity of hot 3*N*-sulphuric acid (239 c.c. for every 100 grams of barium salt) is then added, and the filtrate from the granular precipitate of barium sulphate gradually deposits the pyromellitic acid in large, colourless crystals. Seventy-five to seventy-eight grams of pyromellitic acid are thus obtained, amounting to 85—88 per cent. of the theoretical quantity, and a further 3 or 4 grams can be obtained by concentrating the mother liquor.

NORTHERN POLYTECHNIC INSTITUTE,
LONDON, N.

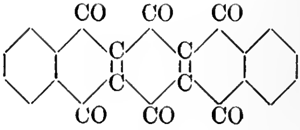
CCXXX.—*The Synthetical Production of Derivatives of Dinaphthanthracene.*

By William Hobson Mills and Mildred Mills.

The knowledge hitherto possessed of $\beta\beta'\beta'$-dinaphthanthracene (I) or of its derivatives is exceedingly scanty:



(I.)

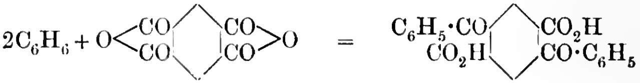


(II.)

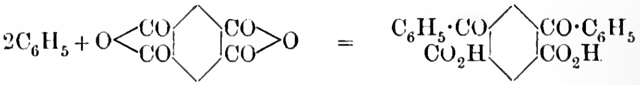
Russig (*J. pr. Chem.*, 1900, [ii], **62**, 30) obtained a dinaphthanthratriquinone (II) by the action of concentrated sulphuric acid on 1:4-dihydroxy-2-naphthoic acid, and this is apparently the only compound hitherto described which can be regarded definitely as a representative of this group.*

In view of the interest which $\beta\beta'\beta'$-dinaphthanthracene possesses as a higher member of the series of hydrocarbons, naphthalene, anthracene, naphthacene—composed of benzene nuclei condensed in straight alinement—we have endeavoured to obtain some more extended knowledge of this hydrocarbon and its derivatives in the hope that it might be possible thereby to gain further insight into the constitution of condensed nuclei of this type.

With this end in view we have attempted to bring about by means of aluminium chloride a reaction between benzene and pyromellitic anhydride analogous to the well known condensation of benzene with phthalic anhydride, which results in the formation of benzoylbenzoic acid. In this manner we have obtained two isomeric dibenzoylbenzenedicarboxylic acids, as shown by the following equations:



(III.)



(IV.)

The constitution of these two acids was established by fusion with potassium hydroxide. The acid of higher melting point and

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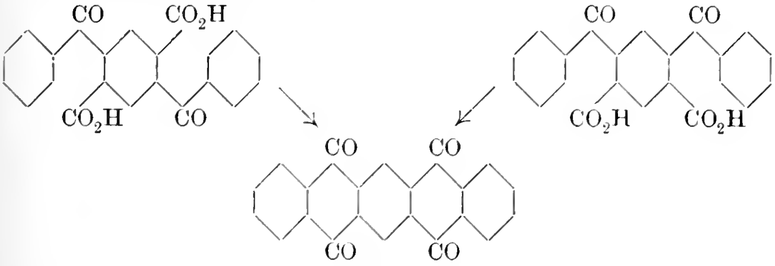
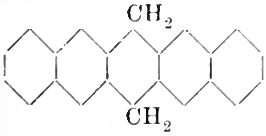
* The question of Russig's dinaphthanthracene (*loc. cit.*, p. 49) is discussed later (p. 2198).

lower solubility undergoes scission under these conditions into benzoic acid and terephthalic acid, and is accordingly *2:5-dibenzoylterephthalic acid* (III). The isomeric acid, being similarly resolved into benzoic acid and *iso*phthalic acid, must have the alternative constitution (IV). Both these acids on being warmed with concentrated sulphuric acid undergo intramolecular condensation with the loss of two molecules of water. The product is in each case the same yellow, crystalline compound of exceedingly high melting point (408° corr.), and from its mode of formation it must necessarily be dinaphthanthradiquinone (V):

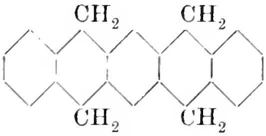


(V.)

From this diquinone it has been possible to prepare a series of derivatives of dinaphthanthracene. In the first place, we attempted to obtain dinaphthanthracene itself by reduction with zinc dust and ammonia, and under these conditions the diquinone is, in fact, converted into a hydrocarbon of very sparing solubility. This is, however, not dinaphthanthracene, but a dihydrodinaphthanthracene* (VI):



(VI.)



(VII.)

As this method of production presented considerable experimental difficulties, and the yield of dihydrodinaphthanthracene was small, we investigated the behaviour of the diquinone towards fuming hydriodic acid and phosphorus, hoping thus to obtain a tetrahydrodinaphthanthracene (VII), from which it might be possible to obtain dinaphthanthracene by oxidation. The product of the reaction was, however, unexpectedly, not a single compound, but a mixture of two isomeric tetrahydrodinaphthanthracenes. The oxidation of the isomeride present in larger quantity (α-tetrahydrodinaphthanthracene) has been carefully studied. The hydro-

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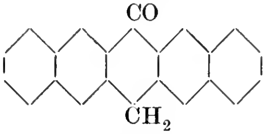
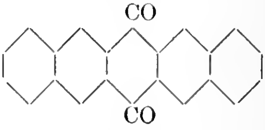
* The constitution of these compounds is discussed later.

carbon was found to be smoothly oxidised by ferric chloride in acetic acid solution, and by means of the regulated action of this reagent a series of oxidation products has been obtained.

The first of these is dihydrodinaphthanthracene (VI), identical with that produced, as stated above, when the diquinone is reduced with zinc dust and ammonia. As the second oxidation product, dinaphthanthracene might have been expected; we have, however, not been able to isolate it, the next substance obtained being dinaphthanthrone (VIII), a golden-yellow compound:



(VIII.)

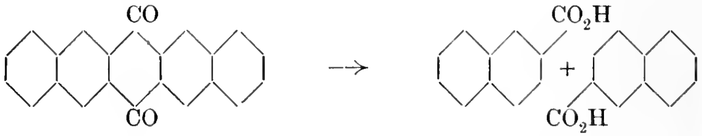


(IX.)

The final product of oxidation by ferric chloride is dinaphthanthraquinone (IX), a yellow substance of very high melting point (389° corr.), which is sharply characterised by the magnificent colour and fluorescence of its solution in concentrated sulphuric acid. When chromic acid is employed for the oxidation of α-tetrahydrodinaphthanthracene, a mixture of dinaphthanthraquinone (IX) and the original dinaphthanthradiquinone (V) results.

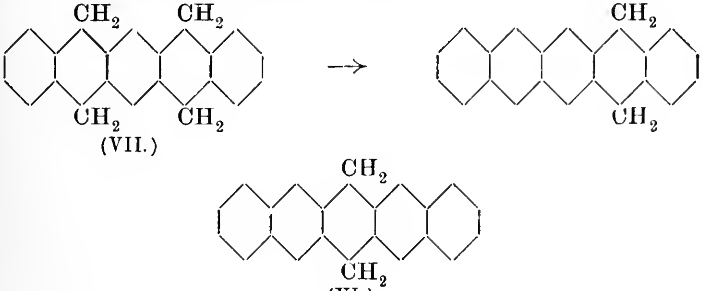
The behaviour of β-tetrahydrodinaphthanthracene on oxidation is very similar. Ferric chloride gives as the first product dihydrodinaphthanthracene (VI), and as the final product dinaphthanthraquinone, whilst chromic acid oxidises it to a mixture of dinaphthanthraquinone and dinaphthanthradiquinone.

The key to the constitution of these oxidation products is the constitution of dinaphthanthraquinone, and this could be readily determined, for, on fusion with sodium hydroxide, the quinone was resolved into two molecules of β-naphthoic acid, and this—in conjunction with its method of formation—is a conclusive proof that



its constitution is correctly represented by formula IX. Further, the position of the oxygen atom in dinaphthanthrone must correspond with that of the oxygen atoms in dinaphthanthraquinone; dinaphthanthrone must accordingly possess the constitution VIII. Finally, the position of the methylene group in dinaphthanthrone must correspond with that of the methylene groups in dihydrodinaphthanthracene, which will thus have the formula VI.

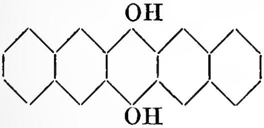
As regards the relationship between the two tetrahydrodinaphthanthracenes, they are certainly not crystallographic modifications, for they differ considerably in stability, and we have not been able to bring about their interconversion. They have the same molecular weight, and since stereoisomerism seems in this case most highly improbable, it is to be concluded that they are structurally isomeric. Unfortunately, their behaviour on oxidation is so similar as scarcely to afford a basis for conclusions as to their constitution. It is, however, probable that one of the two isomerides must have the formula VII (corresponding with that of the diquinone from which they are formed), although the production from it of symmetrical dihydrodinaphthanthracene on oxidation would necessitate the assumption of intramolecular transformation of the primarily formed unsymmetrical product:



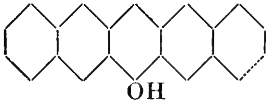
(VII.)

(VI.)

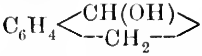
It is of some interest that dinaphthanthraquinone is sharply differentiated from anthraquinone and naphthacenequinone, in that it gives no coloration with sodium hydroxide and zinc dust; that is to say, it is not converted into dinaphthoxanthranol (X) under conditions under which the corresponding change is readily brought about in the case of anthraquinone and naphthacenequinone. Moreover, dinaphthanthrone, unlike anthrone, is neither converted into dinaphthanthranol (XI) by alkalis, nor does it yield the acetyl derivative of that compound with acetic anhydride:

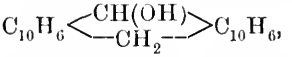


(X.)



(XI.)

These facts appear to indicate that considerable resistance is opposed to the passage of dihydrodinaphthanthracene derivatives into compounds containing the true dinaphthanthracene nucleus, and the difference between dihydroanthracene and dihydrodinaphthanthracene as regards the readiness with which they can be converted into their parent hydrocarbons is probably due to this cause, dihydroanthranol,  $C_6H_4<\genfrac{}{}{0pt}{}{CH(OH)}{CH_2}>C_6H_4$ (which is to be regarded as the primary oxidation product of dihydroanthracene), undergoing dehydration much more rapidly than it can be oxidised to anthrone, whilst in dihydrodinaphthanthranol,



$$C_{10}H_6<\genfrac{}{}{0pt}{}{CH(OH)}{CH_2}>C_{10}H_6,$$

the tendency to lose the elements of water is so small that the further oxidation product, dinaphthanthrone, alone can be isolated.

Russig, in his paper quoted above, refers to a hydrocarbon having the composition of a dinaphthanthracene, which he obtained by distilling dinaphthanthratriquinone with zinc dust, and consequently regarded as $\beta\beta\beta'\beta'$-dinaphthanthracene (*loc. cit.*, p. 49). This hydrocarbon was further investigated by Hartenstein (*Diss.*, Jena, 1892), who obtained from it by oxidation with chromic acid a quinone having the composition $C_{22}H_{12}O_2$, to which, without further confirmation, he assigned the formula (IX), which we have shown to be that of the dinaphthanthraquinone described in the present communication. From Hartenstein's description, however, his compound is undoubtedly different from ours; its melting point is more than 180° lower, and he describes it as dissolving in sulphuric acid with a purple colour, whereas the colour of the solution of our dinaphthanthraquinone in sulphuric acid is an intense pure blue, with a magnificent crimson fluorescence, which could not possibly escape notice. Moreover, if the hydrocarbon of Russig and Hartenstein were really $\beta\beta\beta'\beta'$-dinaphthanthracene, it would be expected to give on oxidation with chromic acid our dinaphthanthraquinone, and possibly also dinaphthanthradiquinone. That the product could be a monoquinone different from ours seems so unlikely that the more probable conclusion would appear to be that the hydrocarbon of Russig and Hartenstein was not $\beta\beta\beta'\beta'$-dinaphthanthracene, but an isomeric hydrocarbon, distillation of the triquinone with zinc dust having brought about some change more profound than simple reduction. It is probable, therefore, that $\beta\beta\beta'\beta'$-dinaphthanthracene is still unknown.

EXPERIMENTAL.

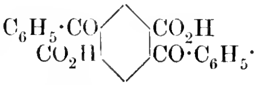
Dibenzoyl-terephthalic and -isophthalic Acids.

Thirty grams of finely ground pyromellitic anhydride are heated with 750 c.c. of benzene and 70 grams of powdered aluminium chloride for three hours in a water-bath at 65—70°. The mixture is then poured on ice, and, after the addition of concentrated hydrochloric acid, is distilled in a current of steam. When the benzene has been completely removed, the acids produced are left in the form of white, granular masses suspended in the hot liquid. These are collected,* washed with water, and dissolved in boiling dilute potassium hydroxide solution. After filtration to remove a little insoluble matter, the acids are reprecipitated with hydrochloric acid.

The weight of the crude mixture of dibenzoyl-terephthalic and -*iso*phthalic acids thus obtained is approximately equal to that of the pyromellitic anhydride taken, corresponding with a yield of about 60 per cent. of the theoretical.

This product may be used without further purification for conversion into dinaphthanthradiquinone.

2:5-*Dibenzoylterephthalic Acid*,



When the crude mixture of acids, obtained as described above, is dissolved in the minimum quantity of boiling glacial acetic acid, the solution after cooling gradually deposits this compound in clusters of fine, white needles, in amount equal to rather more than half that of the mixed acids taken. After recrystallisation from glacial acetic acid or dilute alcohol it melts at 319—320°. It crystallises with one molecule of water:

0·4894 (air-dried) lost, at 135°, 0·0214. $H_2O = 4·4$.
$C_{22}H_{14}O_6,H_2O$ requires $H_2O = 4·6$ per cent.

0·3306 † gave 0·8527 CO_2 and 0·1110 H_2O. C = 70·34; H = 3·73.
$C_{22}H_{14}O_6$ requires C = 70·59; H = 3·74 per cent.

The acid dissolves readily in acetone, and is rather soluble in alcohol. It is moderately soluble in boiling glacial acetic acid, but almost insoluble in benzene or chloroform. It is characterised by a sparingly soluble *sodium* salt.

Half a gram of the acid was fused for three hours with 10 grams of potassium hydroxide at 275°. The fusion was then dissolved in water and acidified with dilute sulphuric acid, when an acid was precipitated which on heating sublimed without previous fusion, and was identified as terephthalic acid by conversion (through the chloride) into its methyl ester. This melted at 140°, both alone and when mixed with pure methyl terephthalate prepared in the usual manner from *p*-toluidine. The filtrate from the terephthalic

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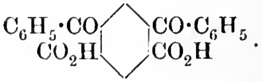
* The filtrate deposits during the course of two or three days the greater part of the pyromellitic acid which has escaped condensation.

† Dried at 135°.

acid on extraction with ether yielded 0·25 gram of an acid readily identified as benzoic acid.

4:6-*Dibenzoyl*iso*phthalic Acid*,



After the separation of the sparingly soluble dibenzoylterephthalic acid from the acetic acid solution of the crude mixture of dibenzoylphthalic acids, the mother liquor is diluted with an equal volume of water. 4:6-*Dibenzoyl*iso*phthalic acid* then separates gradually in well-formed crystals in the course of a few days.

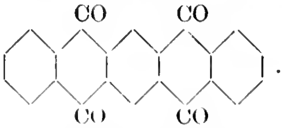
After purification by recrystallisation from dilute acetic acid or dilute alcohol, it melts at 277—278°:

0·3801 gave 0·5368 CO_2 and 0·0716 H_2O. C=70·7; H=3·8.
$C_{22}H_{14}O_6$ requires C=70·6; H=3·7 per cent.

The acid dissolves very readily in acetone, alcohol, glacial acetic acid, or ether. In benzene or chloroform it is practically insoluble. It crystallises far less readily than the isomeric acid, and tends to separate as an oil.

One gram of the acid was fused for two and three-quarter hours with 18 grams of potassium hydroxide, the temperature being kept as nearly as possible at 275°. The fusion was dissolved in water, and the solution, after filtration, acidified and extracted with ether. The residue after evaporation of the ether weighed 1·05 grams. It was boiled twice with 8 c.c. water, and the undissolved portion was crystallised twice from dilute alcohol. An acid was thus obtained crystallising in very fine needles, which melted at 328—329°, and then sublimed. A specimen of *iso*phthalic acid melted at the same temperature, as did also the mixture of the two substances. As a confirmation, the acid was converted into its methyl ester by warming with methyl-alcoholic hydrogen chloride. The ester melted at 65—66°, and its melting point was not depressed by the addition of methyl *iso*phthalate. Pure benzoic acid was separated from the portions which had dissolved in boiling water by sublimation in a vacuum at 100°.

5:7:12:14-*Dinaphthanthradiquinone*,



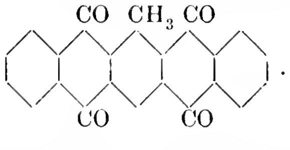
The mixture of dibenzoyl-*iso*phthalic and -terephthalic acids, obtained as described above, is dissolved in concentrated sulphuric acid in the proportion of 8 c.c. to each gram of the mixed acids, and the resulting deep yellowish-brown liquid is heated in a boiling-water-bath for four to five hours. On keeping—sometimes even during the heating—the mixture sets to a mass of excessively fine, long, yellow, flexible, silky needles, which are so asbestos-like that filtration can be effected on a filter disk, without using filter paper, the substance forming its own filter. After having been collected, the quinone is washed with glacial acetic acid, finally with water, and then dried. A further quantity can be obtained by pouring tho sulphuric acid mother liquor into 10 volumes of water, and adding excess of sodium hydroxide. The finely divided yellow precipitate thus produced is allowed to settle, the supernatant liquid is syphoned off, and the quinone collected and washed. The total yield is about 95 per cent. of the theoretical.

Dinaphthanthradiquinone is very sparingly soluble in most organic media, even at the boiling temperature. It can be best recrystallised from boiling nitrobenzene or pyridine, separating in bright yellow needles. The melting point is 408° (corr.),* the substance being apparently quite stable up to this temperature. Small quantities can readily be sublimed:

0·1971 gave 0·5652 CO_2 and 0·0547 H_2O. C = 78·2; H = 3·0.
$C_{22}H_{10}O_4$ requires C = 78·1; H = 3·0 per cent.

It gives a golden-yellow solution in concentrated sulphuric acid. When heated with sodium hydroxide solution and zinc dust a deep brownish-red colour is developed, which disappears on shaking with air. When boiled with glacial acetic acid, tin, and a drop of concentrated hydrochloric acid, a bluish-mauve solution is produced.

13-*Methyl*-5 : 7 : 12 : 14-*dinaphthanthradiquinone*,



Anhydrous *s*-dibenzoyluvitic acid (Mills and Easterfield, Trans., 1902, **81**, 1321) is dissolved in concentrated sulphuric acid (4 c.c. for every gram), and heated for six to seven hours in a boiling-water bath. The deep golden-yellow solution gradually becomes dark brown. After cooling, it is poured on ice, rendered alkaline with sodium hydroxide (the production of an alkaline reaction is marked by the appearance of a slight blue coloration), and the mixture

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* The determinations of the melting points of this compound and of dinaphthanthraquinone were determined in a bath composed of an equimolecular mixture of sodium and potassium nitrates.

heated for twelve hours on a water-bath. The supernatant liquid can then be readily syphoned off, the precipitate washed once by decantation, collected, and washed.

This compound is very sparingly soluble in the usual solvents at the boiling temperature. It can be recrystallised from nitrobenzene, from which it separates in yellow needles showing no sharp melting point, but decomposing between 298° and 304°:

0·1218 gave 0·3495 CO_2 and 0·0397 H_2O. C=78·3; H=3·3.
$C_{23}H_{12}O_4$ requires C=78·4; H=3·4 per cent.

A deep brownish-red colour is produced when the substance is heated with zinc dust and sodium hydroxide solution.

α- and β-Tetrahydrodinaphthanthracene.

A mixture of two parts of dinaphthanthracenediquinone with one part of red phosphorus is heated in sealed tubes for forty-eight hours with hydriodic acid (D 1·9) to 120—130°, 3 grams of the mixture and 10 c.c. of hydriodic acid being placed in each tube. After opening the tubes, water is added, and the solid products are collected and well washed with water, and, if necessary, with sulphurous acid. If the reduction has been carried out at 115—120°, an appreciable quantity of an intermediate product of red colour will be present, which, since it has phenolic properties, is best removed by boiling out once or twice with a mixture of equal volumes of alcohol and a 20 per cent. aqueous solution of sodium hydroxide, which dissolves it, forming a greenish-blue solution. On acidification of this solution the red compound is recovered, and can be fully reduced by a second heating with phosphorus and hydriodic acid. Reduction at temperatures above 135°, on the other hand, leads to loss through the formation of more highly reduced products. The residue left after the removal of the above-mentioned red compound is almost colourless. It is dried and crystallised from boiling benzene, which removes the higher reduction products. The substance obtained in this way is manifestly a mixture, melting between 237° and 250°. Attempts to effect a separation by fractional crystallisation from various solvents were fruitless. It was found, however, that on boiling with a quantity of amyl alcohol insufficient for complete solution (30 c.c. of amyl alcohol for each gram of substance) and filtering hot, the compound of higher melting point was concentrated in the residue, and that of lower melting point crystallised from the filtrate almost pure. By one or two repetitions of this process, the mixture can be resolved into two substances, one crystallising in lustrous platelets melting at

240—241°, the other in needles melting at 270° with some decomposition (turning pink from about 240° upwards).

The relative quantities of the two substances depend on the temperature employed in the reduction—the lower this temperature the larger the proportion of the compound melting at 270°; but this always forms the smaller part of the product, and if the reduction is carried out at 135° or over, none of it can be isolated.

The substance melting at 240—241° is *a-tetrahydrodinaphthanthracene*:

0·2034 gave 0·6995 CO_2 and 0·1148 H_2O. C=93·8; H=6·3.
$C_{22}H_{18}$ requires C=93·6; H=6·4 per cent.

The compound of higher melting point is the isomeric *β-tetrahydrodinaphthanthracene*:

0·1842 gave 0·6296 CO_2 and 0·1027 H_2O. C=93·2; H=6·5.
$C_{22}H_{18}$ requires C=93·6; H=6·4 per cent.

Since the formation of bimolecular products is not uncommon in the reduction of substances containing the carbonyl group, and the difference in composition between a tetrahydro- and a bistrihydro-derivative lies not far without the limits of analytical error, it seemed desirable to satisfy ourselves that these substances were really isomeric by determining their molecular weight.

The molecular weight of α-tetrahydrodinaphthanthracene was determined by the ebullioscopic method:

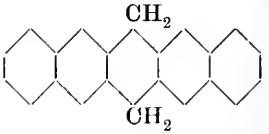
0·0745 in 6·4 c.c. benzene gave E=0·13. M.W.=287.
0·0708 „ 5·63 „ „ „ E=0·16. M.W.=258.
0·0716 „ 6·1 „ „ „ E=0·145. M.W.=270.
0·0721 „ 5·1 „ „ „ E=0·16. M.W.=289.
$C_{22}H_{18}$ requires M.W. 282.

β-Tetrahydrodinaphthanthracene was found to be too sparingly soluble in boiling benzene to give accurate results by this method. Its molecular weight was accordingly determined cryoscopically in naphthalene:

0·1007 in 17·9 naphthalene gave $\Delta t=-0·142$. M.W.=273.
0·2049 „ 17·9 „ „ $\Delta t=-0·279$. M.W.=283.
$C_{22}H_{18}$ requires M.W. 282.

Both compounds with concentrated sulphuric acid containing a trace of nitrosylsulphuric acid give an amethyst-purple coloration, which slowly passes into olive-green.

6 : 13-*Dihydrodinaphthanthracene*,



The production of this compound by oxidation of tetrahydrodinaphthanthracene is most successfully carried out in small quantities.

To a boiling solution of 0·4 gram of α-tetrahydrodinaphthanthracene in 200 c.c. of glacial acetic acid, a solution of 0·7 gram of anhydrous ferric chloride in 70 c.c. of glacial acetic acid is added drop by drop during the course of three-quarters of an hour. The boiling is continued two hours after the addition of the ferric chloride is complete, and crystals of the sparingly soluble product frequently separate during the heating. The crude substance contains much unoxidised tetrahydrodinaphthanthracene, which is removed by extracting twice with 25 c.c. of boiling glacial acetic acid. Since the tetrahydrodinaphthanthracene is deposited almost quantitatively from the filtrate and can be treated again with ferric chloride, the final yield is satisfactory. By recrystallising twice from pyridine the new hydrocarbon is obtained in a state of purity. It separates in small crystals, which form a colourless, lustrous, felted mass on the filter. It decomposes in the neighbourhood of its melting point, beginning to turn pink at 295°, and melting between 300° and 310°, the exact temperature depending on the rate of heating:

0·2232 gave 0·7706 CO_2 and 0·1167 H_2O. C=94·2; H=5·8.
$C_{22}H_{16}$ requires C=94·3; H=5·7 per cent.

This compound is much less soluble in boiling benzene and boiling acetic acid than are the tetrahydrodinaphthanthracenes, and on protracted boiling with solvents like amyl alcohol and xylene, in which it is more soluble, it turns mauve. It is readily recrystallised from pyridine. It can be sublimed in small quantities, but becomes thereby partly transformed into a purple substance. It dissolves in concentrated sulphuric acid, giving a solution of a pale yellow colour, gradually deepening to orange-brown, and finally becoming green. In concentrated sulphuric acid containing a trace of nitrosylsulphuric acid it gives the same coloration as the tetrahydro-compounds, namely, an amethyst-purple, which passes slowly into green.

Dihydrodinaphthanthracene is also obtained when β-tetrahydrodinaphthanthracene is oxidised with ferric chloride in acetic acid solution in the manner described above.

Production of Dihydrodinaphthanthracene from Dinaphthanthradiquinone by Reduction with Zinc Dust in Alkaline Suspension.

To 5 grams of the diquinone suspended in 250 c.c. of 20 per cent. sodium hydroxide solution was added a zinc-copper couple, prepared by grinding zinc dust (10 grams) with a little concentrated ammonia, and adding gradually an ammoniacal solution of basic cupric chloride.

The mixture was heated for thirty-six hours in a water-bath, contact with air being prevented by a mercury valve, and four or five further quantities of zinc-copper couple, each prepared from 5 grams of zinc dust, were added in ammoniacal suspension through a tap funnel.

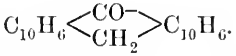
The deep reddish-brown colour, which appears at first, gradually fades, and the solution finally becomes nearly colourless. It must be filtered as far as possible with exclusion of air, since it contains a substance rapidly oxidised by atmospheric oxygen with the formation of a dark blue precipitate. To remove any of the latter which may have been produced during the filtration the solid residue is again heated with sodium hydroxide solution, when the blue compound is reduced to its phenolic precursor by the excess of zinc dust present. The solid is then collected, the zinc and zinc hydroxide dissolved with hydrochloric acid, and the dried residue extracted with 300 c.c. of benzene. The substance left on evaporation of the benzene after crystallisation from pyridine should be colourless. If, however, the above-mentioned oxidation product has been incompletely removed, the crystals will have a red colour. This impurity can be removed by cautious washing with concentrated sulphuric acid. The hydrocarbon thus obtained was found on comparison to be identical with the dihydrodinaphthanthracene produced by oxidation of the α- and β-tetrahydro-compounds. The yield barely exceeded 10 per cent. of the theoretical.

The blue insoluble substance formed by atmospheric oxidation of the colourless intermediate product was also examined. On acidification it gave reddish-purple flocks, which seemed to undergo alterations on heating with organic solvents. It was therefore acetylated, 2 grams being heated with 30 c.c. of acetic anhydride and a few drops of sulphuric acid for one hour in an oil-bath at 140°. The solution became yellow, and the orange-yellow acetyl derivative crystallised on cooling. After several recrystallisations from glacial acetic acid, it was obtained in aggregates of rather short, reddish-orange needles, melting not very sharply at 255°. The analysis corresponded with a compound of the formula $C_{22}H_{14}O_2(C_2H_3O_2)_2$:

0·2004 gave 0·5326 CO_2 and 0·0739 H_2O. C=73·0; H=4·1.
$C_{22}H_{16}O_6$ requires C=73·2; H=4·2 per cent.

It thus appears to be the diacetyl derivative of a dihydroxytetrahydrodinaphthanthraquinone.

Dinaphthanthrone,



$$C_{10}H_6 < \genfrac{}{}{0pt}{}{CO-}{CH_2} > C_{10}H_6.$$

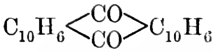
A solution of five parts of anhydrous ferric chloride in acetic acid and a little water is allowed to drop during the course of two hours into a boiling solution of one part of α-tetrahydrodinaphthanthracene in 1000 parts of glacial acetic acid. Crystals of the sparingly soluble dihydrodinaphthanthracene usually separate during the addition of the ferric chloride, but redissolve as the oxidation proceeds. The heating is continued for one and a-quarter hours after the whole of the ferric chloride has been added. From the cold solution brown crystals are slowly deposited, which are collected after two or three days, and purified by repeated crystallisation from pyridine.

Dinaphthanthrone is obtained in this way in golden-yellow, highly lustrous platelets, which melt at 271—273°. It is rather more soluble in the common solvents at their boiling points than dinaphthanthraquinone:

0·1787 gave 0·5869 CO_2 and 0·0759 H_2O. C=89·6; H=4·7.
$C_{22}H_{14}O$ requires C=89·8; H=4·8 per cent.

The behaviour of the substance towards sulphuric acid is characteristic. On the addition of sulphuric acid containing a trace of nitrosylsulphuric acid, the crystals turn brown, and slowly dissolve to form a brown solution, which on warming becomes green. If water is now cautiously added, the green passes over into a beautiful deep blue.

Dinaphthanthraquinone,



$$C_{10}H_6 < \genfrac{}{}{0pt}{}{CO}{CO} > C_{10}H_6.$$

A solution of twenty-two parts of anhydrous ferric chloride in eight to ten times its weight of acetic acid containing a little water is added slowly drop by drop to a boiling solution of one part of α-tetrahydrodinaphthanthracene in 500 parts of glacial acetic acid. Crystals of dihydrodinaphthanthracene appear after a short time, but gradually redissolve. The boiling is continued for two hours after the addition of the ferric chloride is complete, and the crystals which separate slowly from the cold solution are collected after twelve to twenty-four hours. Their weight is approximately equal to that of the tetrahydrodinaphthanthracene taken. After having been two or three times recrystallised from pyridine, the quinone is obtained pure in flattish, yellow needles, which melt at 388—389°

(corr.), and are very sparingly soluble in the common solvents. It can be sublimed in small quantities:

0·1246 gave 0·3925 CO_2 and 0·0471 H_2O. C=85·9; H=4·2.
0·2063 „ 0·6458 CO_2 „ 0·0729 H_2O. C=85·4; H=3·9.
$C_{22}H_{12}O_2$ requires C=85·7; H=3·9 per cent.

This compound remains unchanged when heated with sodium hydroxide solution and zinc dust. Its most characteristic property is that of dissolving in concentrated sulphuric acid with the formation of a solution of most striking appearance; intensely blue by transmitted light, crimson by reflected light, the true colour of the solution being in the latter case masked by the powerful red fluorescence. The absorption spectrum of this solution contains two bands in the visible region; one in the yellowish-green, the other in the red, the approximate boundaries of which in dilute solutions are wave-lengths 5610—5820 and 6120—6420 respectively. The band in the red is the more persistent and sharply defined. The fluorescent spectrum consists of a single red band, extending approximately from wave-length 6210 to 6740, and accordingly overlapping the lower two-thirds of the absorption band in the red. The fluorescence is excited chiefly by the part of the spectrum which lies between the outer limits of the two absorption bands and most powerfully by the region of the band in the red. Blue or violet light produces no visible effect.

On the addition of a little water the blue solution becomes cherry-red, and the fluorescence disappears.

The scission of dinaphthanthraquinone into two molecules of β-naphthoic acid was carried out as follows: The finely-powdered substance was added to molten potassium hydroxide heated to 275°, and the mixture kept at this temperature for one hour. A certain quantity of naphthalene was produced, the odour of naphthalene being perceptible, especially towards the commencement of the operation.* After cooling, the chocolate-brown fused [illegible] was dissolved in water, and sulphuric acid gradually added, when the solution was nearly neutral a dark, flocculent substance was precipitated. After removal of this, the liquid on acidification deposited an acid which, having been recrystallised from dilute acetic acid, melted at 181—182°, the melting point of β-naphthoic acid.

A mixture of the acid and β-naphthoic acid melted also at this temperature:

0·1706 was neutralised by 9·96 c.c. N/10-sodium hydroxide solution.
$C_{10}H_7{\cdot}CO_2H$ requires 9·92 c.c.

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* Dinaphthanthraquinone is easiy converted into naphthalene by heating with soda-lime in a small ignition tube.

It was further converted into its methyl ester by heating with methyl alcohol and sulphuric acid. In appearance, odour, and melting point (77°) the ester agreed exactly with a specimen of methyl β-naphthoate prepared for comparison. The mixed melting point was also 77°.

Oxidation of Tetrahydrodinaphthanthracene with Chromic Acid.

To a boiling solution of one part of α-tetrahydrodinaphthanthracene in 350 parts of glacial acetic acid was added drop by drop during one and three-quarter hours a solution of 1·9 parts of chromium trioxide in a little water and 100 parts of acetic acid, and the mixture was then boiled for ten minutes longer. On cooling, bright yellow crystals separated, the weight of which was 80—85 per cent. of the hydrocarbon taken. These crystals were a mixture of dinaphthanthraquinone and dinaphthanthradiquinone, the former of which was isolated by boiling the mixture with sodium hydroxide solution and zinc dust, when the diquinone passed into solution as the red sodium salt of the oxanthranol-like reduction product, and the monoquinone was left undissolved, whilst the diquinone was obtained in a state of purity by repeatedly extracting the mixture with small quantities of boiling acetic acid (which removed most of the monoquinone), and crystallising the residue from pyridine. Analysis showed that the product was a dinaphthanthradiquinone:

0·1748 gave 0·4994 CO_2 and 0·0488 H_2O. C = 77·9; H = 3·1.
$C_{22}H_{10}O_4$ requires C = 78·1; H = 3·0 per cent.

The melting point and mixed melting point, 408° (corr.), conclusively proved its identity with the original diquinone.

The oxidation of β-tetrahydrodinaphthanthracene was carried out in the same manner, with similar results.

Part of the expense of this work was defrayed by a grant from the Research Fund of the Chemical Society, for which the authors desire to express their thanks.

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CCXXXI.—*The Essential Oil of Cocoa.*

By James Scott Bainbridge and Samuel Henry Davies.

In the older literature it is always assumed that the aromatic substance in cocoa is either identical with cocoa-red or associated with it. Cocoa-red, the colouring matter of fermented cocoa, was shown by Hilger and Lazarus (*Apoth. Zeit.*, 1892, **7**, 469) and by Schweitzer (*Pharm. Zeit.*, 1898, **43**, 389) to be obtained by splitting up the cocoa glucoside, which is stated to be resolved into one molecule of cocoa-red, six of dextrose, and one of theobromine. There is, however, nothing in the composition of cocoa-red to suggest an aromatic substance with a powerful flavour, and it is natural to assume that the distinctive flavour and aroma in this, as in all similar seeds, might be due to the presence of an essential oil. Again, cocoa-red, when prepared in a pure state, appears to be absolutely devoid of flavour. This was established beyond doubt by W. A. Caspari in this laboratory in 1901–2. Repeated attempts were then made to isolate an essential oil. It was found that the odour of cocoa clung with extraordinary persistence to the spirit used for extracting it. The spirit reacted decidedly with Schiff's reagent, but it was impossible to isolate the flavour by treatment with sodium hydrogen sulphite or phenylhydrazine. An aqueous distillate of the cocoa was also impregnated with cocoa flavour, but this was not persistent like the flavour in spirit. At that time, attempts to distil larger quantities of cocoa and to isolate the essential oil from the distillate with benzene were unsuccessful, the material isolated principally consisting of fatty acids.

In 1908 Dr. J. Sack, of the Government Agricultural Laboratory in Surinam, in the course of an article on the fermentation of cocoa (*Inspectie van den Landbouw in West Indie*, Bulletin 10, Jan., 1908) described the distillation of pulverised fermented cocoa with steam, whereby a small amount of an essential oil was obtained possessing the aroma and flavour peculiar to cocoa. Twenty kilograms of cocoa are said to have yielded 1 c.c. of oil, which, however, does not appear to have been further investigated.

We have subsequently carried out the distillation of large quantities of cocoa nibs, and have succeeded in obtaining sufficient of the essential oil for the investigation described in this communication. There can be no doubt that the material isolated was a true essential oil; it possessed an intense odour of cocoa, and the flavour was clearly perceptible in a dilution of 1 in 50 million parts of dilute syrup. The flavour is most nearly akin to that of coriander oil.

Before dealing in detail with the physical and chemical examination of the oil, we may point out that the method of preparing cocoa beans in the tropics by fermentation and slow drying, adds to the number of possible ethereal substances present in the crude oil. To explain this, we must briefly refer to the method of fermentation practised in South America and the West Indies.

The cocoa-pods are cut open, the contents scooped out and conveyed into large tanks or boxes, where the sweet, viscous pulp, in which the beans are embedded, ferments and forms a thin alcoholic and acid liquor, which largely drains away.

The first runnings from a fermenting box in Jamaica, taken fifteen hours after the pods were broken, had the following composition:

Specific gravity, 1·023.

	Percentage by weight.
Total solids	5·75
Ash	0·51
Reducing sugars (as invert sugar)	3·5
Pectin	1·97
Alcohol	4·88
Total acidity (as acetic acid)	0·78
Volatile acid (,, ,,)	0·58
Nitrogen	0·05

The ash consists chiefly of sodium, potassium, and calcium carbonates and phosphates.

The non-volatile acid consists largely of tartaric; no succinic, citric, or malic acid could be detected. No sucrose is present.

Part of this liquor penetrates into the beans, which are thus saturated with the products of fermentation, but the shell membrane is fine enough to prevent the micro-organisms from percolating to the kernels.

The course of fermentation may be briefly described from unpublished observations made by one of us in the West Indies.

The beans and adherent pulp, which are commonly at a temperature of 26—28° when placed in the fermenting box, rapidly become warmer. During the first twenty-four hours the temperature rises to 35° or 40°, varying with the exact position in the box. Within forty-eight hours it rises to 40—45°, and if the fermentation is continued for five or six days the temperature will be found to rise to a maximum of 45—50°. Higher temperatures are occasionally noted, but they rarely exceed 53°. If the fermentation is continued for the exceptionally long period of ten to eleven days, as is the custom on certain Trinidad estates, the temperature will fall slightly towards the close. It is customary to transfer the contents of the fermenting boxes from one box to another every two or three days. Some form of false bottom is provided, and the cover is loose, so that partial aeration goes on throughout the process. The quantity of cocoa dealt with in each box represents, on an average, the contents of 8000 to 16,000 pods, or 12—24 cwt. of wet material. The outside of the bean changes from white or pale pink to rich brown; characteristic odours are evolved, and a vigorous fermentation takes place. The stages of this fermentation may be distinguished thus:

First, a large growth of *Saccharomyces apiculatus*, together with small quantities of *Saccharomyces anomalus*, etc., doubtless derived from the surface of the pod husks. This stage lasts about twelve hours.

Secondly, as in spontaneous wine fermentation, an enormous development of true *Saccharomyces* occurs, exhibiting typical oval and round cells. If the temperature rises normally, no formation of new cells is noted after the first forty-eight hours. The alcohol produced soon arrests the growth of *Sacch. apiculatus* and the "wild" yeasts. A quantity of alcoholic liquor drains away.

The third stage of fermentation is characterised by a very large growth of acetic acid bacteria, a great number being carried to the fermenting boxes by swarms of the "vinegar fly" (*Drosophila*). The drainings now consist of a dilute vinegar. The complete mixing of the mass every second or third day ensures the presence of these organisms in every part of the fermenting mass. If the temperature does not rise above 50°, the acetic bacteria continue to grow during the remainder of the fermentation.

A fourth stage is reached if the fermentation is prolonged beyond eight days, when a growth of spore-bearing bacilli of the *Bacillus subtilis* type becomes evident.

In addition to these successive fermentations it will be found that when the cocoa is turned out from the fermenting boxes and dried slowly in the sun, as is often the case, a modified fermentation takes place at night, so long as the beans are sufficiently moist, and large colonies of wild yeast and bacteria become visible on the surface of the beans.

With the advance of fermentation the change of odour is marked; the sweet, fruity, and alcoholic odour of the early stage changes to a strongly alcoholic, and this to an ethereal odour suggesting ethyl acetate. Later a strong acetic acid odour supervenes, but this is always accompanied by fruity and ethereal components. Finally, if the fermentation is prolonged and putrefactive organisms predominate, an odour resembling that of high game is evolved.

It is obvious that a number of the products resulting from these complex fermentations will percolate into the bean, and of these the less volatile constituents will remain in the dry kernel. Consequently we shall expect to find that the true essential oil of cocoa is accompanied by a certain number of esters and higher alcohols, analogous to those produced in other spontaneous fruit fermentations taking place at comparatively high temperatures in presence of a free supply of air.

Isolation of Essential Oil.

Our first experiments were carried out with fermented Trinidad cocoa beans of good quality. A preliminary experiment was made with raw, and a second with roasted beans, using quantities of 150 kilos. The amount of crude oil obtained from 150 kilos. of cocoa was 4 to 5 c.c., obviously insufficient for fractional distillation. After successive trials with 250 and with 1000 kilos., we finally subjected 2000 kilos. of cocoa to distillation in 100 kilo. lots.

The cocoa employed in the final experiment is known in commerce as "Arriba"; it represents the best fermented product of Ecuador. It was chosen on account of its strong aromatic and spicy flavour, suggesting an exceptionally large content of essential oil. The beans were lightly roasted, the shell removed by the ordinary nibbing process, and the warm nibs, without being ground, were subjected to pressure in hydraulic presses to remove as much cocoa-butter as possible. The cake was carefully broken up to avoid reducing it to a fine powder, so that it presented a porous substance through which steam could readily percolate.

The crushed nibs were then submitted to a steam distillation, using clean steam, superheated to an average temperature of 120°. For each charge of 100 kilos. about 40 litres of water were condensed at the rate of 20 litres per hour; this was immediately shaken with specially purified light petroleum (b. p. 25—38°), and the shaking out repeated a second time. The petroleum extracts were collected and concentrated (at 25—27°/500—550 mm.) from a volume of 55 litres to 3½ litres. This was dried over calcium chloride, concentrated to half a litre, washed repeatedly with *N*/2-potassium hydroxide, then with water, and several times with *N*/2-sulphuric acid, finally removing every trace of acid by washing with water. The residual light petroleum was then removed in a vacuum. In this way 24 grams of oil were obtained from 2000 kilos. of cocoa, a quantity not exceeding 1 part in 100,000 of the original cocoa beans.

The oil obtained from the preliminary experiment had a specific gravity of 0·9075 at 15° and refractive index of 1·4728 at 20°. It contained no sulphur, and gave the following numbers on analysis: C = 75 57; H = 10·45; N = 1·3. The oil was subjected to repeated fractional distillation in a vacuum.

Trustworthiness of Method of Distillation.

In order to determine whether all the essential oil had been separated under the conditions of our distillation, we submitted a batch of cocoa, already exhausted with steam in the usual way, to a rapid treatment with superheated steam. Ninety per cent. of the distillate proved to be free fatty acid, and the unsaponifiable oil, which had a marked lemon-grass odour, represented only 0·09 gram per 1000 kilos. of cocoa; a negligible quantity.

We also treated an exhausted batch of cocoa with 1 per cent. of its weight of sulphuric acid, and then submitted it to a rapid treatment with highly superheated steam (128°) with the view of hydrolysing any ester of high boiling point which might not have volatilised in the first steam distillation.

From 75 kilos. of cocoa, 0·408 gram of a pale yellow oil was obtained, which had a very penetrating odour suggesting valeric acid and cocoa. It was found to consist of: (*a*) a non-acidic substance, presumably cocoa oil, weighing only 0·027 gram, a quantity too small for investigation, and (*b*) an acid which proved to be hexoic. (Found, $C=62·0$; $H=10·0$. $C_6H_{12}O_2$ requires $C=62·03$; $H=10·34$ per cent.) As hexoic acid is known to be formed when cocoa-butter is distilled with steam, we may conclude that our method of distillation removes practically the whole of the essential oil.

In the aqueous distillate, after extraction with light petroleum, the presence of ethyl alcohol, acetic, propionic and butyric acid was proved. These are undoubtedly the products of the fermentation of the cocoa bean.

Alkaline Solution.

The oil in solution in light petroleum was washed four times with 25 c.c. of $N/2$-potassium hydroxide in an atmosphere of nitrogen, light being excluded. The alkaline solution was saturated with carbon dioxide and extracted with light petroleum, from which 0·201 gram of octoic acid was obtained. (Found, $C=66·64$; $H=11·27$. $C_8H_{16}O_2$ requires $C=66·66$; $H=11·11$ per cent.) The alkaline solution was acidified and distilled in a current of steam, and the residue extracted with light petroleum, from which valeric acid was obtained. (Found, $C=60·48$; $H=9·59$. $C_5H_{10}O_2$ requires $C=58·83$; $H=9·8$ per cent.) The steam distillate had an odour of butyric acid; it yielded an acid, which by analysis of the silver salt proved to be a mixture of octoic and *n*-nonoic acids.

We conclude that the free acids in cocoa-oil consist of valeric, octoic, *n*-nonoic, and possibly hexoic acids.

Acid Solution.

The oil solution was then washed with *N*/2-sulphuric acid, from which 0·085 gram of a yellow oil with a disagreeable, pungent odour was obtained. It contained 10 per cent. of nitrogen, but was not further examined.

Absence of Primary Alcohols.

All the light petroleum extracts of cocoa-oil were dried over calcium chloride, which was then dissolved in much water, and distilled in a current of steam. No alcohol could be detected in the distillate, and this was taken as evidence that no primary alcohol was present in the oil.

Fractional Distillation of Purified Oil.

The light petroleum solution of the purified oil was distilled in a small Claisen flask. When practically all the petroleum had been removed, the flask was connected to a Brühl receiver, the whole placed under a vacuum, and the remaining air displaced by nitrogen. The oil was then distilled and twice redistilled, and the final fractions were kept in the dark in closed tubes filled with nitrogen.

The residues from the first and second fractional distillations were subjected to a very high temperature to separate any esters of high boiling point such as benzyl benzoate, but even at 205°/7·5 mm. no distillate could be recovered, whilst the residue was frothing and evidently decomposing. The portion of the residue soluble in alcohol was extracted with light petroleum, and washed with sodium carbonate to remove the acid. The acid, the silver salt of which was moderately soluble in water, was extracted and purified by conversion into the sodium salt, and proved to be octoic acid. (Found, C=68·17; H=10·92. $C_8H_{16}O_2$ requires C=66·66; H=11·11 per cent.)

The non-acidic substances were probably oxygenated decomposition products.

Fraction (1), which weighed 0·51 gram, and boiled at 49—53°/21 mm., with a refractive index of 1·4299, had a pleasant ethereal odour suggestive of certain amyl esters:

0·1799 gave 0·4276 CO_2 and 0·1617 H_2O. C=64·8; H=10·0 per cent.

The analytical numbers are, by a coincidence, near those required by amyl acetate (C=64·61; H=10·77 per cent.), but on saponification, 0·231 gram required 9·54 c.c. *N*/10-potassium hydroxide, giving an ester number of 231; this corresponds with only 53·6 per cent. of amyl acetate. The products of saponification proved to be: (*a*) acetic acid, and (*b*) a mixture of amyl alcohol, and an unsaponifiable oil with a lemon-grass odour.

Fraction (2), which weighed 1·51 grams, and boiled at 57—70°/19·5—15·5 mm., with a refractive index of 1·4529, had an odour resembling that of the previous fraction, but with a stronger infusion of the lemon-grass substance:

0·2052 gave 0·4891 CO_2 and 0·1715 H_2O. C=65·0; H=9·29 per cent.,

a result resembling fraction (1).

On saponification an ester number of 150 (corresponding with 39 per cent. of amyl acetate) and acid number of 26·5 were recorded. The products of saponification were: (*a*) an insoluble acid, which proved to be octoic, (*b*) a soluble acid consisting of a mixture of acetic and propionic acids, and (*c*) an alcohol which could not be completely separated from the accompanying unsaponifiable oil; its boiling point (130—138°) and characteristic odour agreed with amyl alcohol.

Fraction (3), which weighed 0·6 gram, boiled at 70—84°/15 mm., and had a refractive index of 1·4688. This is an intermediate fraction, still containing a considerable proportion of the fermentation esters, but a larger proportion of the main constituents of the oil. The acid number was 37·6, and the ester number, 93·7, was equivalent to 22 per cent. of amyl butyrate. The products of saponification include (*a*) an insoluble acid, the barium salt of which gave an analysis approximating to *n*-nonoic acid, (*b*) a soluble acid, in too small quantity for analysis, yielding an ethyl ester with a marked odour of ethyl butyrate, and (*c*) unsaponifiable, consisting of a small quantity of a yellow oil with a mixed "amyl" and cocoa odour.

0·294 Gram was acetylated, and 0·138 of the resulting oil required 5·3 c.c. *N*/10-potassium hydroxide to saponify it, yielding an acetylation number of 215·2, which with an ester number of 93·7 gave an alcohol number of 121·5. This is equivalent to 33 per cent. alcohol, $C_{10}H_{18}O$, in the original oil (see fraction 5).

Oxidation Products.—The unsaponifiable matter and alcohol were extracted, mixed with the similar products of saponification of the oil [(*c*) above], and oxidised with potassium dichromate and sulphuric acid in excess. The liquor, after being rendered alkaline, was freed from the remaining oil and distilled. The distillate was found to contain acetone (*p*-bromophenylhydrazone, m. p. 89—91°). The residue was acidified, and the insoluble acid extracted with ether. This consisted of 0·028 gram of white crystals mixed with some oil, and the analysis of the barium salt indicated a mixture of octoic and lævulic acids.

A further oxidation of the neutral product gave a minute quantity of white solid, melting below blood-heat, probably consisting of impure lævulic acid (m. p. 33°). The soluble volatile acid was distilled off, and the analysis of the barium salt indicated that it was a mixture of acetic and propionic acids. (Found, Ba=50·0. Calc., Ba=53·7 and 48·4 per cent. respectively.)

We conclude that the products of oxidation are acetone, acetic and propionic acids, lævulic and *n*-nonoic acids.

Fraction (4), which weighed 9·7 grams, boiled at 87—97°/11—15 mm., and had a freezing point below −16°; its refractive index was $1\cdot4658_{20^\circ}$, specific gravity 0·8936 15°/15°, and the specific rotation $[\alpha]_D^{20} + 11^\circ 36'$. A qualitative test showed the absence of sulphur.

This was the middle and most important fraction, and constitutes with (5) the bulk of the oil. Its odour, whilst resembling that of cocoa, was also reminiscent of coriander and lemon-grass:

0·2284 gave 0·6335 CO_2 and 0·2233 H_2O. C=75·63; H=10·86.
0·2534 „ 0·7020 CO_2 „ 0·2485 H_2O. C=75·56; H=10·90.
0·20 „ 0·9 N_2 at 21° and 766 mm. N=0·52.

The molecular weight was determined by the cryoscopic method with benzene as solvent.

It was found that the molecular weight increased with concentration, which suggests association of the solute; to obtain a true result, very dilute solutions were used:

0·0382 in 9 of benzene gave $\Delta t = -0\cdot148$. M.W.=143.
0·0786 „ 9 „ „ $\Delta t = -0\cdot291$. M.W.=150.
0·1195 „ 9 „ „ $\Delta t = -0\cdot439$. M.W.=151.

The true molecular weight may be taken to be about 150. The property of association in solution points to the probable presence of tertiary alcohols.

No ketone or aldehyde was present, and the oil was not changed by treatment with sodium amalgam for twenty-four hours.

Oxidation by permanganate in acid solution gave acetone and propionic acid, and by ammoniacal silver oxide, valeric acid.

2·003 Grams of oil were acetylated, and 0·514 of the resulting oil required 3·1 c.c. of *N*/2-potassium hydroxide to saponify it. This gave an acetylation number of 170·8, which with an ester number of 33 (see below) gave an alcohol number of 137·8, which is equivalent to 42 per cent. of an alcohol, $C_{10}H_{18}O$ (see fraction 5), in the original fraction.

2·04 Grams of oil required 1·0 c.c. *N*/2-potassium hydroxide to neutralise, giving an acid number of 13·7, and 2·4 c.c. *N*/2-potassium hydroxide to saponify, giving an ester number of 33.

The products of saponification include: (*a*) an insoluble acid, which on analysis of the barium salt proved to be octoic acid; (*b*) a soluble acid, which proved to be butyric acid; and (*c*) a neutral constituent, which resembled the original fraction in odour and elementary composition. This formed the bulk of the oil, and indicated that the main constituent is unaffected by saponification. It was then oxidised with potassium dichromate and sulphuric acid, and the products were found to include acetone (*p*-bromophenylhydrazone, m. p. 90—92°), propionic, *n*-nonoic, and valeric acids, together with 0·6 gram of a yellow oil, which had an odour suggesting impure citral or methylheptenone. A very small quantity of an impure semicarbazone was prepared, but this only served to prove the presence of an aldehyde or ketone. By means of the bisulphite compound, a minute quantity of methylheptenone was obtained, but the main constituent passed into solution, probably as the disulphonate of citral; this was later proved to be the case by an approximate analysis of the compound. The small quantities dealt with make identification extremely difficult, but we believe the products of oxidation to be citral and possibly methylheptenone, acetone, propionic, *n*-nonoic, and valeric acid.

The results of bromination will be found under fraction (5).

Fraction (5), which weighed 3·1 grams, and boiled at 97—99°/10 mm. (b. p. = 210°/760 mm.), had a refractive index of 1·4660. In odour it resembled fraction (4); it was somewhat greener when fresh, but darkened on keeping:

0·2081 gave 0·5608 CO_2 and 0·2003 H_2O. C = 73·49; H = 10·67 per cent.

On saponification, 0·494 gram required 0·2 c.c. *N*/2-potassium hydroxide to neutralise, giving an acid number of 11·0, and 0·5 c.c. *N*/2-potassium hydroxide to saponify, giving an ester number of 28·6. The products of saponification were found to consist of hexoic and propionic acids, together with unsaponifiable matter which was submitted to oxidation (see below).

A portion of the oil was acetylated, and 0·476 gram of esterified oil required 3·5 c.c. *N*/2-potassium hydroxide to saponify, giving an acetylation number of 207·8, which, with an ester number of 28·6, gave an alcohol number of 179·2. This corresponds with 57 per cent. of linalool (see below) in original fraction. Experiments with pure linalool show that it is not readily acetylated, and that only 80 per cent. of it forms an ester under the conditions of the experiment. This agrees with observations made by Gildemeister and by Parry. It is therefore necessary to add 25 per cent. to the quantity of linalool determined by acetylation, to get an approximate idea of the amount actually present. This would give 71 per cent. of linalool in fraction (5).

The neutral product of the saponification was oxidised with potassium dichromate and sulphuric acid, using the equivalent of one atom of oxygen per molecule of alcohol. The oxidation proved to be incomplete, and butyric acid alone was identified amongst the products.

A phenylurethane derivative of the alcohol was prepared, using 0·5 gram of oil. After purification, the compound was found to consist of white crystals melting at 55—59° (linaloolphenylurethane melts at 64—66°). (Found, C=76·0; H=8·7; N=5·8. Linaloolphenylurethane requires C=74·7; H=8·44; N=5·1 per cent.) The experiment was repeated with double the quantity of oil, and white needles separated, which melted at 60—61°, but the bulk of the material was very impure and contained N=6·4 per cent. Although the above agreement is poor, we may conclude that linalool is the main alcohol of fraction (5), and doubtless also of fraction (4). This is confirmed by comparing the physical constants of fraction (4) with *d*-linalool:

		d-Linalool, $C_{10}H_{18}O$.	Cocoa oil, fraction (4).
Gildermeister *	b. p. at 760 mm.	198—199°	195—210° (calc.)
	,, 13 ,,	88·3—89·5°	87— 97 (15—11 mm.)
	D^{15}................	0·870	0·8936
	n_D^{20}	1·4668	1·4658
Schmidt †	$[\alpha]_D^{20}$	+13°19′	+11°36′
(for coriandrol)	M.W.	154	150 (approx.)

* *Arch. Pharm.*, 1895, **233**, 179.

† *Ber.*, 1898, **31**, 834.

As a further proof of the presence of linalool it was proposed to acetylate the alcohol and separate the resulting geranyl acetate from the other constituents by distillation. The esterification was carried out in the usual way on 1·0 gram of oil, and the product fractionally distilled under diminished pressure. The middle fraction, boiling at 100—104°/4—2·5 mm. (b. p. 240°/760 mm. approx.), had an odour resembling that of geranyl acetate. (Found, C=70·23; H=9·44. $C_{12}H_{20}O_2$ requires C=73·47; H=10·2 per cent.) On saponification, 0·11 gram required 0·85 c.c. *N*/2-potassium hydroxide, giving an ester number of 235, corresponding with only 82 per cent. of geranyl acetate. This accounts for the poor agreement of the combustion figures.

The degree of unsaturation was determined by the bromine absorption in carbon tetrachloride solution; a parallel experiment was carried out on pure linalool. Cocoa-oil required per gram for substitution 1·092 grams, and for saturation 1·092 grams of bromine, whilst linalool required 0·752 gram and 1·673 grams respectively. This determination is far from exact, but allowing for the fact that the oil is estimated to contain 71 per cent. of an alcohol, it is sufficient to prove that this alcohol has two double bonds.

Although the small quantities dealt with prevent exact individual determinations, the cumulative evidence of the presence of linalool is conclusive.

Thus cocoa-oil must be added to the considerable number of essential oils containing linalool, of which coriander, bergamot, neroli, ylang ylang, and linaloe are amongst the best known.

Fraction (6), which weighed 1·35 grams and boiled at 100—109°/10 mm., had a refractive index of 1·4707. It was darker in colour, and had a somewhat harsher odour than (4) and (5), which suggested the beginnings of decomposition:

0·246 gram gave 2·2 c.c. N_2 at 24° and 762 mm. N=1·01 per cent.

On saponification, 0·467 gram required 3·0 c.c. of 0·742 N/10-potassium hydroxide to neutralise, giving an acid number of 26, and 5·6 c.c. of 0·947 N/10-potassium hydroxide to saponify, giving an ester number of 62. This is double the ester number of fraction (5); the increase might be due to the presence of linaloyl acetate. 0·629 Gram was acetylated, and 0·5 gram of the esterified oil required 16·3 c.c. of 0·947 N/10-potassium hydroxide to saponify, giving an acetylation number of 172·8, which, with an ester number of 62, gave an alcohol number of 110·8. This is equivalent to 30·5 per cent. of linalool in the original fraction. Among the products of saponification, impure octoic acid was identified. The unsaponifiable was expected to consist chiefly of linalool (or geraniol). 0·577 Gram was oxidised with potassium dichromate and sulphuric acid, and 0·211 gram of an oil was obtained, which had a pleasant odour of thyme, closely resembling that of methylheptenone. From this a semicarbazone was prepared, which, on purification, melted at 132—134°. Methylheptenonesemicarbazone melts at 136—137°. We may conclude that methylheptenone is an oxidation product; acetone was also identified, both being derived from linalool.

Fraction (7), which weighed 0·67 gram, and boiled at 109—116°/9—7·5 mm., had a refractive index of 1·4861. It was obviously decomposed, the odour being very flat and harsh. A series of unsuccessful experiments was made on this and other fractions to elucidate the composition of the nitrogenous substance.

Nitrogenous Constituent of Oil.

In preliminary experiments, repeated washing with acid and alkali failed to remove the nitrogenous substance. An attempt was made to free fraction (3), which contained N = 0·94 per cent: (*a*) by boiling for two hours with 20 per cent. sodium hydroxide, but this only reduced the nitrogen to 0·65 per cent.; (*b*) by boiling for half an hour with 50 per cent. sulphuric acid; but this had still less effect, reducing the nitrogen to 0·73 per cent.

The purer oil of the final experiment contained less nitrogen, the two lower-boiling fractions of the final distillation none at all, the largest fraction (4) 0·52 per cent., fraction (6) 1·01 per cent., and the residue 1·8 per cent. Fraction (7), treated with stannous chloride and hydrochloric acid for an hour, gave a small quantity of amine, but the resulting material still contained N = 3·4 per cent. Again, the residue from the second fractionation, after boiling with concentrated hydrochloric acid for six hours, still retained N = 1·1 per cent. We conclude that there might be a small proportion of a nitro-compound present, but we were unable to throw any light on the composition of the main nitrogenous constituent.

Summary.

(1) The aromatic principle of the cocoa bean is an essential oil.

(2) Two thousand kilos. of cocoa nibs (deprived of some cocoa-butter) gave a yield of 24 c.c. of purified oil with a very powerful aroma and flavour of cocoa.

(3) The oil was fractionally distilled three times, and the third distillation yielded seven fractions.

(4) The early fractions were rich in esters, derived in all probability from the fermentation of the cocoa bean.

(5) The middle fractions were rich in *d*-linalool, corresponding closely with coriandrol.

(6) The amount of esters and of linalool may be estimated from the following table. Twenty-five per cent. of the amount of linalool determined by acetylation has been added in each case. The total linalool represents more than 50 per cent. of the cocoa oil.

Fractions.	Approx. calc. b. p./760 mm.	Weight in grams.	Percentage of esters.	Percentage of *d*-linalool.
1	140°	0·51	54 as amyl acetate	Not determined
2	165	1·51	39 as amyl propionate	25
3	175—190°	0·6	22 as amyl butyrate	41
4	195—210	9·7	10 as hexyl (?) butyrate ...	53
5	210°	3·1	7 as hexyl (?) propionate...	71
6	220—230	1·35	22 as linaloyl acetate (?) ...	38
7	230—240	0·67	Not determined	Not determined

(7) In addition to the esters and linalool, from 4 to 10 per cent. of octoic acid (with hexoic and *n*-nonoic) was found in the different fractions.

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THE COCOA WORKS,
YORK.

CCXXXII.—*The Constituents of* Cluytia similis.

By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

THE small shrub, *Cluytia hirsuta*, Muell. Arg., belonging to the *Euphorbiaceae*, is reputed in South Africa to be of value as an antidote for anthrax and for the disinfection of "milt-ziek," or anthrax-infected meat, and is apparently much used by the natives for this purpose (Smith, "A Contribution to South African Materia Medica," Cape Town, 1895, p. 57). This author also mentions, as being more valuable than the above-mentioned species, a smaller form of *Cluytia*, which is either a variety of *C. hirsuta* or else a distinct species. A quantity of this smaller species, which grows in the open veldt, attaining a height of 10 inches or less, was therefore specially collected for us by Mr. G. E. Oliver, of East London. The identity of this material has been determined by Mr. Hutchinson, of Kew, through the kindness of Mr. E. M. Holmes, F.L.S., as *Cluytia similis*, Muell. Arg.

Mr. Oliver also ascertained that the root of *Cluytia similis* was eaten by certain of the natives as an antidote for snake-bite poisoning, and a quantity of this material, as well as the above-ground portions of the plant, has therefore been submitted to examination.

EXPERIMENTAL.

I.—*Examination of the Stems and Leaves.*

The material employed in this investigation consisted of the entire above-ground portions of *Cluytia similis*, Muell. Arg., which had been specially collected in South Africa.

Test for an Alkaloid.—A quantity (20 grams) of the finely-ground, dried material was digested with Prollius's fluid, and the resulting extract subjected to the usual tests for an alkaloid, but with a negative result. In view of the statement of Smith (*loc. cit.*) that this species of *Cluytia* gave a "green reaction" with chlorine water and ammonia, thus indicating the presence of quinine or an allied alkaloid, the last-mentioned test was repeated, but with a negative result.

Preliminary Extraction of the Plant.—A quantity (25 grams) of the dried and crushed material was extracted successively in a Soxhlet apparatus with various solvents, the following amounts of extract, dried at 100°, being obtained:

Petroleum (b. p. 35—50°)	extracted	0·83 gram	= 3·32	per cent.
Ether	,,	0·34 ,,	= 1·36	,,
Chloroform	,,	0·22 ,,	= 0·88	,,
Ethyl acetate	,,	0·41 ,,	= 1·64	,,
Alcohol	,,	2·52 ,,	= 10·08	,,
	Total =	4·32 grams	= 17·28	per cent.

For the purpose of a complete examination a quantity (7·42 kilograms) of the crushed and dried material was extracted by continuous percolation with hot alcohol, when, after the removal of the greater part of the solvent, 2·17 kilograms of a dark-coloured extract were obtained.

The entire amount of the above-mentioned extract was mixed with water, and steam passed through the mixture for several hours, when a quantity (1·24 grams) of an essential oil was removed. This oil possessed a pale yellow colour and a strong, rank odour.

After the distillation of the extract with steam, as above described, there remained in the distillation flask a dark brown, aqueous liquid (*A*) and a quantity of dark green resin (*B*). The latter was separated, and repeatedly washed with boiling water, the concentrated washings being added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

The aqueous liquid (*A*) was concentrated somewhat, and extracted ten times with ether, the ethereal liquids being united, washed, and evaporated to a small bulk. A large volume of petroleum (b. p. 35—50°) was then added to the residue, after which the clear liquid was separated by decantation from the precipitated resinous material. The petroleum solution was then evaporated, the residue dissolved in ether, and the resulting solution shaken successively with aqueous ammonium and sodium carbonates and potassium hydroxide.

Isolation of Chrysophanol, $C_{15}H_{10}O_4$.

The material soluble in ammonium carbonate was small in amount, and consisted chiefly of amorphous products. It also contained, however, an acid soluble in warm water, which gave a violet coloration with ferric chloride, and appeared to be salicylic acid. The sodium carbonate extract was very small, and was discarded, but on acidifying the extracts obtained by means of potassium hydroxide a quantity (0·15 gram) of a substance was obtained, which separated from ethyl acetate in golden-coloured leaflets. This substance melted at 191°, and proved to be chrysophanol (compare Trans., 1911, **99**, 948). (Found, C = 70·6; H = 4·1. Calc., C = 70·9; H = 3·9 per cent.) It yielded diacetylchrysophanol, melting at 206°. This occurrence of chrysophanol is remarkable, for, so far as known to the present authors, it is the first recorded instance of an anthraquinone derivative occurring in a euphorbiaceous plant, and, moreover, it is very unusual to find this substance unassociated with emodin monomethyl ether.

The portion of the ethereal extract of the aqueous liquid which was undissolved by petroleum consisted only of amorphous products, together with a trace of chrysophanol.

The original aqueous liquid (*A*) which had been extracted with ether was then shaken with twenty successive portions of amyl alcohol. The amyl alcohol solution so obtained, when evaporated to a small bulk under diminished pressure, deposited a quantity (30 grams) of an amorphous, yellow solid. This product could not be crystallised, but after heating with dilute sulphuric acid it yielded a small amount of a sugar which gave *d*-phenylglucosazone, thus indicating that a little glucosidic substance was present.

Isolation of a New Acid, $C_{10}H_{10}O_4$.

The remainder of the amorphous solid which separated from the amyl alcohol extracts on concentration, as above described, was boiled for one minute with 10 per cent. aqueous potassium hydroxide, after which the mixture was acidified and extracted with ether. The ethereal solution was washed, and shaken successively with aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide. The material removed by the last-mentioned two alkalis consisted only of amorphous products, but the product obtained on acidifying the ammonium carbonate extract slowly crystallised on keeping. The solid so obtained was crystallised from benzene containing a small proportion of ethyl acetate, when a quantity (0·08 gram) of a substance separated in pale brown, prismatic needles, which melted without decomposition at 159°:

0·0790 gave 0·1794 CO_2 and 0·0377 H_2O. C = 61·9; H = 5·3.

$C_{10}H_{10}O_4$ requires C = 61·9; H = 5·2 per cent.

A further and larger amount of this acid was obtained by the alkaline hydrolysis of the product yielded by the lead subacetate precipitate, as subsequently described, when it was again analysed, and the above-given result fully confirmed. The only known compound with which this acid agrees at all in its properties is 2:5-dihydroxy-β-methylcinnamic acid, which is stated to melt at 155—156° (*Ber.*, 1907, **40**, 2731). A quantity of the latter acid was therefore synthesised, but it was found not to be identical with the acid here described. It is evident, therefore, that the above-mentioned *acid* melting at 159° is a new compound; it yields a brown-coloured solution when treated with ferric chloride, which, on keeping, becomes turbid.

The original amyl alcohol filtrate from the amorphous solid, the investigation of which has just been described, contained a quantity of amorphous material which was soluble in water. This product was thoroughly investigated, and submitted to hydrolysis, both with acid and alkali, but nothing crystalline could be obtained from it.

The original aqueous liquid (*A*), which had been extracted with amyl alcohol, as above described, was freed from this solvent and treated with an excess of basic lead acetate solution. A very bulky, yellow precipitate was thus produced, which was collected and washed.

Isolation of Fumaric Acid.

The basic lead acetate precipitate, which was found to contain a considerable amount of lead chloride owing to the presence of potassium chloride in the original aqueous liquid, was decomposed by means of hydrogen sulphide, and filtered. The filtrate was then evaporated to a small bulk under diminished pressure, and extracted with ether in order to remove any ether-soluble substances which had been formed by the hydrolysing action of the hydrochloric acid derived from the lead chloride. The ethereal liquid so obtained was then extracted successively with aqueous ammonium carbonate, sodium carbonate, and potassium hydroxide. On acidifying the liquid obtained by means of the first-mentioned alkali, and extracting it with ether, a small amount of a brown-coloured product was obtained. The latter, when crystallised from a mixture of ethyl acetate and alcohol, yielded small, light brown prisms, which sublimed at about 200°, and were identified as fumaric acid. (Found, C=41·6; H=3·7. Calc., C=41·4; H=3·4 per cent.)

The sodium carbonate extract, obtained as above described, yielded nothing but amorphous material, but on acidifying the potassium hydroxide extract a small amount of chrysophanol was obtained.

To the original acid aqueous liquid which had been extracted with ether as above described, potassium hydroxide was added until it contained about 8 per cent. of this alkali, when it was boiled for a short time, acidified, and again extracted with ether. The ammonium carbonate extract of the ethereal solution then yielded about 0·5 gram of the previously-described new acid, $C_{10}H_{10}O_4$, which was analysed. (Found, C = 61·8; H = 5·3. Calc., C = 61·9; H = 5·2 per cent.) The remainder of the material dissolved by the ether consisted only of amorphous products.

The filtrate from the lead subacetate precipitate, obtained as above described, was concentrated, when, on keeping, it deposited some potassium chloride and sodium acetate. It furthermore readily yielded *d*-phenylglucosazone (m. p. 216°), but no other definite compound could be obtained from it.

Examination of the Resins (B).

The resin (*B*) was a hard, dark green mass, and amounted to 350 grams, being thus equivalent to about 4·7 per cent. of the weight of the drug employed. It was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a large Soxhlet apparatus with light petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

Isolation of a New Ester, Cluytyl Cluytinate, $C_{49}H_{98}O_2$.

The petroleum extract of the resin was dark green, and, when deprived of solvent, amounted to 207 grams. It was digested with 2 litres of ether, and the mixture kept for some time, and filtered. A quantity (9 grams) of a dark green solid was thus separated, which was washed with ether and then distilled under diminished pressure, when the greater part of the material passed over at a very high temperature as a light-coloured distillate. The latter, which solidified on cooling, was crystallised from glacial acetic acid with the employment of animal charcoal. Two fractions were thus obtained, one of which was very sparingly soluble, and was separated by rapid filtration from the warm solution. This solid was repeatedly crystallised from various solvents, when the melting point remained unchanged at 76·5°. The *substance* formed nacreous leaflets, and amounted to 0·5 gram:

0·0758 gave 0·2266 CO_2 and 0·0932 H_2O. C = 81·5; H = 13·7.

$C_{49}H_{98}O_2$ requires C = 81·9; H = 13·6 per cent.

This compound was found to be a new *ester* formed by the combination of cluytyl alcohol and cluytinic acid, two new compounds described below, and is therefore *cluytyl cluytinate.*

Isolation of Cluytyl Alcohol, $C_{28}H_{57}\cdot OH$, *and Cluytinic Acid,* $C_{20}H_{41}\cdot CO_2H$.

A quantity of cluytyl cluytinate was hydrolysed by boiling with alcoholic potassium hydroxide for two hours, after which water was added and the alkaline mixture extracted with ether. The ethereal liquid was evaporated, when a quantity of an alcohol was obtained, which crystallised from ethyl acetate in small, glistening leaflets, melting at 82·5°, and this melting point was unchanged by further recrystallisation:

0·0942 gave 0·2826 CO_2 and 0·1204 H_2O. C=81·8; H=14·2.

$C_{28}H_{58}O$ requires C=82·0; H=14·1 per cent.

This alcohol thus appears to be a new compound, and it is proposed to designate it *cluytyl alcohol*. A further and larger amount of it was subsequently obtained from the unsaponifiable matter contained in the petroleum extract of the resin, when its properties and composition were confirmed. *Cluytyl acetate*, $C_{28}H_{57}\cdot O\cdot CO\cdot CH_3$, was prepared by the action of acetic anhydride on the respective alcohol, when it formed small leaflets melting at 64°.

The alkaline aqueous liquid from which the cluytyl alcohol had been removed by means of ether, as above described, contained a quantity of a sparingly soluble potassium salt. This was collected, and heated with dilute sulphuric acid and chloroform, after which the chloroform solution was separated, washed, and evaporated, when a solid of low melting point was obtained. The latter was crystallised several times from ethyl acetate, when it formed colourless, lustrous leaflets, melting sharply at 69°. Further crystallisations from alcohol and from glacial acetic acid failed to effect any change in the melting point:

0·0865 gave 0·2446 CO_2 and 0·1013 H_2O. C=77·1; H=13·0.

$C_{21}H_{42}O_2$ requires C=77·3; H=12·9 per cent.

This substance possessed all the attributes of homogeneity, and thus appears to be a new fatty acid possessing the formula $C_{20}H_{41}\cdot CO_2H$, which it is proposed to designate *cluytinic acid*. A further and larger quantity of the same acid was subsequently obtained by the fractional distillation of the esters of the fatty acids present in the petroleum extract, as described below, when its composition and properties were confirmed.

Cluytinic acid has approximately the same melting point as stearic acid, and is indistinguishable in appearance from the latter, but when the two substances are mixed fusion occurs at 61—62°.

The material more readily soluble in glacial acetic acid, from which the above-described cluytyl cluytinate had been separated, was found to consist chiefly of cluytyl alcohol, and was examined in connexion with the unsaponifiable matter described below.

The original ethereal solution from which the crude cluytyl cluytinate had been separated was shaken with aqueous ammonium carbonate, but nothing was removed. It was then shaken with aqueous potassium carbonate, when a quantity of a viscid, green product separated, which was found to consist essentially of cluytyl alcohol. The ethereal liquid was subsequently washed with water, and after separating the dark green aqueous liquid, the former was extracted with aqueous potassium hydroxide, when 0·8 gram of chrysophanol was removed. After this treatment the ethereal liquid was again washed with water, when a further amount of green material was removed, and was found to be similar in character to that removed by water after extraction with potassium carbonate. Both these liquids were acidified, extracted with ether, and the resulting material, which consisted of chlorophyll and free fatty acids, esterified with methyl alcohol. The resulting esters, after being deprived of a large amount of chlorophyll by shaking first with aqueous alkali and subsequently with water, were distilled, and examined in connexion with the esters of the combined fatty acids subsequently described.

Isolation of Cerotic Acid, $C_{27}H_{54}O_2$.

The ethereal solution of the neutral portion of the petroleum extract of the resin was evaporated, and the residue heated for two hours with an excess of alcoholic potassium hydroxide. Water was then added, and the mixture repeatedly extracted with ether. During this operation a quantity of a flocculent solid separated at the juncture of the aqueous and ethereal layers. This was collected, when it was found to consist chiefly of the potassium salt of a higher fatty acid. It was freed from some neutral material, and the fatty acid isolated and crystallised from ethyl acetate. Small, glistening leaflets were thus obtained, which melted at 82—83°. Analysis indicated this substance to be cerotic acid, although the melting point observed is somewhat higher than that usually recorded for this acid. (Found, C=78·7; H=13·3. Calc., C=79·0; H=13·2 per cent.)

The ethereal solution of the unsaponifiable matter, which had been separated from the alkaline, aqueous liquid and the potassium cerotate as above described, was washed, dried, and evaporated, when the residue (25 grams) was dissolved in alcohol. On cooling the solution a quantity (about 5 grams) of an apparently amorphous product separated. This was distilled under diminished pressure, the distillate dissolved in pyridine, and the mixture heated with an equal weight of phthalic anhydride for a short time. Water was then gradually added to the warm solution, and the resulting liquid extracted with ether. The ethereal solution was deprived of pyridine, and then shaken with aqueous sodium carbonate, when a quantity of the solid sodium salt of an acid phthalic ester of an alcohol separated. The latter was collected and hydrolysed with alcoholic potassium hydroxide, when a quantity (2·5 grams) of an alcoholic substance was obtained. The latter formed small, glistening leaflets, melting at 82·5°, and proved to be cluytyl alcohol.

Isolation of Triacontane, $C_{30}H_{62}$.

The ethereal solution from which the sodium salt of the cluytyl hydrogen phthalate had been separated was evaporated, and the residue crystallised, first from ethyl acetate, and subsequently from petroleum (b. p. 90—120°), when a quantity (1 gram) of colourless leaflets was obtained. This substance melted at 65·5°, and was found to be triacontane, $C_{30}H_{62}$. (Found, C = 84·9; H = 14·6. Calc., C = 85·3; H = 14·7 per cent.)

Isolation of a New Phytosterol, Cluytiasterol, $C_{27}H_{43}·OH$.

The alcoholic solution of the unsaponifiable matter, from which the crude mixture of triacontane and cluytyl alcohol had been separated, was concentrated, and some ethyl acetate and a little water added. On keeping the mixture for a few days a quantity (0·7 gram) of large, colourless leaflets separated. This product had the properties of a phytosterol, and melted at 136°, but, as it did not appear homogeneous, it was converted into the acetyl derivative. The latter crystallised in leaflets, melting at 131—132°, but, after repeated crystallisation from alcohol and ethyl acetate alternately, the melting point was raised to 139°, at which point it remained constant. The pure acetyl derivative was then hydrolysed, and the resulting alcohol isolated and crystallised from a mixture of ethyl acetate and dilute alcohol, when a quantity (0·35 gram) of colourless leaflets, melting at 159°, was obtained:

0·0942,* on heating at 110°, lost 0·0043 H_2O. $H_2O = 4·6$.
0·0899 † gave 0·2769 CO_2 and 0·0947 H_2O. C = 84·0; H = 11·7.
$C_{27}H_{44}O,H_2O$ requires $H_2O = 4·5$ per cent.
$C_{27}H_{44}O$ requires C = 84·4; H = 11·5 per cent.

This substance was evidently a phytosterol, since it gave the colour reactions exhibited by this class of compounds, and, as it does

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* Air-dried substance. † Dried at 110°.

not agree in its properties with any compound previously described, it is proposed to designate it *cluytiasterol*. Its optical activity was determined with the following result:

0·2853,* made up to 20 c.c. with chloroform, gave α_D $-1°30'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-52·6°$.

Examination of the Fatty Acids.

The alkaline aqueous liquid from which the unsaponifiable matter had been removed, as above described, was acidified, and distilled with steam, but the amount of volatile acid removed was negligible. The mixture was then extracted with ether, when a small amount of an undissolved solid was collected. The latter crystallised from alcohol in needles melting at 248°, and yielded an acetyl derivative melting at 255°, but the amount obtained was too small for further examination. The dark green, ethereal solution containing the fatty acids was then evaporated to a small bulk and treated with a large volume of petroleum (b. p. 35—50°), when the greater part of the chlorophyll was precipitated. The clear petroleum solution was then decanted, evaporated, and the residual fatty acids converted into their methyl esters and distilled, when a quantity (21 grams) of a liquid was obtained. The latter was mixed with the 16 grams of esters previously isolated, and the whole fractionally distilled several times under 60 mm. pressure, when the following fractions were obtained: (i) $-240°$; (ii) 240—250°; (iii) 250—260°; (iv) 260—270°; (v) 270—280°; (vi) 280°+.

Fraction (i) solidified on cooling, and was found to consist of methyl palmitate, since it yielded palmitic acid (m. p. 63°) on hydrolysis. (Found, $C=74·7$; $H=12·5$. Calc., $C=75·0$; $H=12·5$ per cent.)

Fractions (ii) and (iii), when hydrolysed, yielded a small amount of a mixture of unsaturated acids, but the greater part of the material was a mixture consisting essentially of palmitic and stearic acids. (Found, $C=75·2$; $H=12·6$. Calc., for $C_{16}H_{32}O_2$, $C=75·0$; $H=12·5$; for $C_{18}H_{36}O_2$, $C=76·1$; $H=12·7$ per cent.)

Fraction (iv) became partly solid on keeping. On hydrolysis it yielded a further quantity of the previously-described new fatty acid, cluytinic acid, $C_{21}H_{42}O_2$, which was identified by its melting point (69°) and by analysis. (Found, $C=77·3$; $H=13·1$. Calc., $C=77·3$; $H=12·9$ per cent.)

Fraction (v) was too small for examination, but fraction (vi), after being hydrolysed and freed from traces of unsaponifiable matter, yielded an acid melting at 74°. The amount of the latter, however, was too small for investigation.

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* Dried at 110°.

Ethereal Extract of the Resin.

Isolation of a New Tetrahydric Alcohol, Cluytianol, $C_{29}H_{46}O(OH)_4$.

The ethereal extract of the resin was dark green, and amounted to 39 grams. A portion of it (about 1 gram) was a black powder, vary sparingly soluble in ether, which was collected and separately examined. This sparingly soluble solid was treated with animal charcoal in pyridine solution, the product which separated on cooling the filtered liquid being then acetylated by boiling with acetic anhydride containing some pyridine. The solution so obtained was concentrated and cooled, when a substance separated in small plates. This solid was recrystallised seven times from alcohol, when small, colourless leaflets, melting constantly at 160°, were obtained:

0·0919 gave 0·2316 CO_2 and 0·0753 H_2O. C=68·7; H=9·1.

$C_{37}H_{58}O_9$ requires C=68·7; H=9·0 per cent.

This substance proved to be the *tetra-acetyl* derivative of a tetrahydric alcohol isomeric with the trihydric alcohol, ipuranol, which it greatly resembles in its general properties. This new alcohol has been designated *cluytianol*, and the above-described substance is therefore *tetra-acetylcluytianol.*

A quantity of tetra-acetylcluytianol was hydrolysed, and the resulting alcohol crystallised from pyridine, when very small, colourless crystals were obtained, which, when heated fairly rapidly, decomposed and melted at 300—305°:

0·0985 gave 0·2628 CO_2 and 0·0929 H_2O. C=72·8; H=10·5.

$C_{29}H_{50}O_5$ requires C=72·8; H=10·5 per cent.

This is the first time that a substance has been isolated which resembles ipuranol and the other related alcohols in its general characters, but contains four hydroxyl groups.

Tetrabenzoylcluytianol, $C_{29}H_{46}O_5(CO{\cdot}C_6H_5)_4$.—A small quantity of cluytianol was benzoylated in pyridine solution, and the resulting compound crystallised from a mixture of chloroform and alcohol, when long, flattened needles, melting at 192°, were obtained:

0·1029 gave 0·2878 CO_2 and 0·0713 H_2O. C=76·3; H=7·7.

$C_{57}H_{66}O_9$ requires C=76·5; H=7·4 per cent.

The ethereal solution of the more readily soluble portion of the ethereal extract of the resin deposited on keeping a further quantity (about 1 gram) of crude cluytianol. The clear ethereal solution of the resin was then shaken with aqueous ammonium carbonate, which removed a quantity of dark green, viscid material, from which nothing crystalline could be obtained. On subsequently shaking the ethereal solution with aqueous potassium hydroxide, however, a red liquid was obtained, which, when acidified, yielded a yellow powder. The latter was collected, when it was found to be almost insoluble in alcohol or ethyl acetate, but crystallised from dilute pyridine in small rosettes of brownish-red needles, which decomposed and melted at 315°. This substance dissolved in concentrated sulphuric acid with a crimson colour, and possessed the properties of a phenolic anthraquinone derivative:

0·0904 gave 0·2134 CO_2 and 0·0331 H_2O. C=64·4; H=4·1.
0·0957 „ 0·2265 CO_2 „ 0·0352 H_2O. C=64·5; H=4·1.
$C_{14}H_{10}O_5$ requires C=65·1; H=3·9 per cent.

After each of these combustions a small amount (about 0·0005 gram) of inorganic residue was left in the boat, which would account for the somewhat low percentage of carbon found.

The only known compound with which the above-described anthraquinone derivative could be identical is a substance described by Tschirch (*Arch. Pharm.*, 1900, **238**, 427), but as this author does not record the melting point of the anthraquinone derivative he obtained it is impossible to say whether the latter is identical with the substance here described.

The substance obtained from *Cluytia similis*, which is probably a trihydroxydihydroanthraquinone, yielded an acetyl derivative, which crystallised in small, yellow needles, melting at 167°.

The neutral portion of the ethereal extract of the resin, from which the above-described substance had been separated, consisted only of amorphous products

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The chloroform extract of the resin was dark green, and amounted to 10 grams. It was thoroughly examined, and was found to consist of amorphous products, together with a small amount of the above-described substance, $C_{14}H_{10}O_5$.

The ethyl acetate extract of the resin amounted to 7 grams, and consisted only of amorphous products.

The alcohol extract of the resin amounted to 72 grams, and was a nearly black powder. It was submitted to both acid and alkaline hydrolysis, but nothing definite could be isolated from it.

II.—*Examination of the Root.*

A portion (10 grams) of the ground root of *Cluytia similis* was subjected to a preliminary test for an alkaloid by digestion with Prollius's fluid, but with a negative result.

Another portion (25 grams) of the ground material was successively extracted with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°)	extracted	0·23 gram	=0·92 per cent.
Ether	,,	0·27 ,,	=1·08 ,,
Chloroform	,,	0·18 ,,	=0·72 ,,
Ethyl acetate	,,	0·15 ,,	=0·60 ,,
Alcohol	,,	1·03 ,,	=4·12 ,,
	Total =	1·86 grams	=7·44 per cent.

For the purpose of a complete examination, a quantity (7·77 kilograms) of the ground root was completely extracted by continuous percolation with hot alcohol, when, after the removal of the greater part of the solvent, 1·54 kilograms of a dark brown extract were obtained. The latter was mixed with water, and distilled with steam, but practically no volatile material was removed by this treatment.

After the steam distillation the mixture remaining in the distillation flask consisted of a dark-coloured, aqueous liquid (*A*) and a dark brown resin (*B*). The aqueous liquid was decanted, and the resin repeatedly washed with warm water, the washings being concentrated and added to the main bulk of the aqueous liquid.

Examination of the Aqueous Liquid (A).

The aqueous liquid (*A*) was repeatedly extracted with ether, and the resulting extract thoroughly examined, but no indication of the presence of a crystalline substance could be obtained. The aqueous liquid was then extracted many times with amyl alcohol, which removed about 6 grams of a yellow, amorphous product similar to that obtained in like manner from the leaves and stems of the plant.

After the extraction with amyl alcohol the aqueous liquid (*A*) was evaporated to a low bulk under diminished pressure, and treated with alcohol until precipitation commenced. On keeping the mixture a quantity (5 grams) of inorganic matter separated, and was collected. This was found to consist chiefly of potassium sulphate, but copper, iron, manganese, aluminium, calcium, strontium, magnesium, and sodium were also present.

The filtrate from the inorganic matter was then deprived of alcohol, diluted with water, and treated with an excess of basic lead acetate solution. Both the precipitate produced by this treatment and the filtrate from it were deprived of lead, and the resulting liquids examined. The material yielded by the lead acetate precipitate consisted of dark brown, amorphous products, which, on alkaline hydrolysis, gave a small amount of a crystalline acid, melting at 186°, whilst the final aqueous liquid appeared to contain chiefly sugar, since it yielded an abundance of *d*-phenylglucosazone (m. p. 216°), but it also contained some copper, which imparted to it a blue colour.

Examination of the Resin (B).

The resin (*B*) was a dark brown mass, and amounted to 311 grams. It was mixed with alcohol, brought on to purified sawdust, and the dried mixture extracted successively in a large Soxhlet apparatus with petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

The petroleum extract of the resin was a green, viscid mass, amounting to 48·5 grams. It was fully examined in a manner analogous to that employed for the examination of the petroleum extract of the resin from the leaves and stems, when it was found to consist of amorphous products, together with palmitic acid (m. p. 62·5°), apparently some stearic acid, a higher fatty acid (m. p. 73°), and a small amount of unsaturated acids. A quantity of cluytiasterol was also present, which was isolated in the form of its *acetate*, melting at 139°:

0·0955 gave 0·2851 CO_2 and 0·0966 H_2O. C = 81·4; H = 11·2.

$C_{29}H_{46}O_2$ requires C = 81·7; H = 10·8 per cent.

The ethereal extract of the resin amounted to 40 grams, and was a dark green, wax-like mass. It was exhaustively examined, but nothing crystalline could be isolated from it.

The chloroform, ethyl acetate, and alcohol extracts of the resin were nearly black, amorphous solids, and amounted to 66, 17, and 70 grams respectively. They were submitted to both alkaline and acid hydrolysis, and the products carefully examined, but nothing definite could be isolated.

Summary.

The results of this investigation may be summarised as follows: The plant regarded by Smith (*loc. cit.*) as probably a small variety of *Cluytia hirsuta*, Muell. Arg., has been identified as *C. similis*, Muell. Arg. All parts of the plant are devoid of alkaloid.

An alcoholic extract of the above-ground portions of the plant, when distilled in a current of steam, yielded a small amount of an essential oil, possessing a strong, rank odour.

From the portion of the extract which was soluble in water there were isolated: (i) Chrysophanol; (ii) a new *acid*, $C_{10}H_{10}O_4$, which forms light brown, prismatic needles, melting at 159°; (iii) fumaric acid; (iv) apparently a trace of salicylic acid. The aqueous liquid furthermore contained a large amount of a sugar, which yielded *d*-phenylglucosazone and a quantity of potassium chloride.

The portion of the alcoholic extract which was insoluble in water was a dark green resin. From this material the following compounds were isolated: (i) A new ester, *cluytyl cluytinate*, $C_{49}H_{98}O_2$ (m. p. 76·5°); (ii) triacontane, $C_{30}H_{62}$; (iii) a new phytosterol, *cluytiasterol*, $C_{27}H_{44}O$, melting at 159°, and having $[\alpha]_D -52·6°$. *Cluytiasteryl acetate* melts at 139°. (iv) *Cluytyl alcohol*, $C_{28}H_{58}O$, m. p. 82·5°; (v) palmitic, stearic, and cerotic acids, together with a small amount of a mixture of unsaturated acids; (vi) a new fatty acid, *cluytinic acid*, $C_{21}H_{42}O_2$ (m. p. 69°); (vii) a new tetrahydric alcohol, *cluytianol*, $C_{29}H_{46}\cdot O(OH)_4$ (m. p. 300—305°). Cluytianol is isomeric with the trihydric alcohol, ipuranol, which it resembles in its general properties. *Tetra-acetylcluytianol* melts at 160°, and *tetrabenzoylcluytianol* at 192°; (viii) a compound, $C_{14}H_{10}O_5$, which is probably a trihydroxydihydroanthraquinone.

The alcoholic extract of the root of *Cluytia similis* consisted chiefly of amorphous material, but it yielded palmitic and stearic acids; a higher fatty acid (m. p. 73°); a small amount of a mixture of unsaturated acids; and a quantity of cluytiasterol. It also contained some inorganic matter, in which the presence of copper, iron, manganese, aluminium, calcium, strontium, magnesium, sodium, and potassium was established.

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CCXXXIII.—*Hydrazoximes of Benzil and Diacetyl.*

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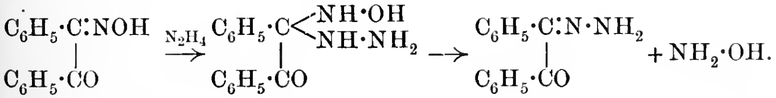
THE expression "hydrazoxime" appears to have been used first by von Pechmann and Wehsarg (*Ber.*, 1888, **21**, 2994) in connexion with derivatives of α-diketones in which one carbonyl group has undergone condensation with hydroxylamine, whilst the other has combined with a substituted hydrazine. The compounds of this class are not numerous, and so far as we have been able to ascertain do not include any unsubstituted hydrazoximes, an aromatic hydrazine having been invariably employed for their production.

The possibilities of stereoisomerism presented by both oximes and hydrazones invite attention to substances which belong simultaneously to these two classes, and we have therefore studied the action of hydrazine hydrate on the monoximes of benzil and diacetyl, but although hydrazoximes are readily produced from these materials, we have not encountered a definite case of isomerism; with diacetyl there is some indication that a very unstable form is the first product, but this changes so readily into the permanent modification that only one class of derivatives was obtainable.

When benzil-α-monoxime is treated with hydrazine hydrate in alcoholic solution, a crystalline product is rapidly formed, but instead of the expected hydrazoxime, this consists of benzilhydrazone, the hydrazine residue having simply displaced the oximino-group. A similar observation was made by von Rothenburg (*Ber.*, 1893, **26**, 2061) in connexion with benzaldoxime and acetoxime, both of which yield the respective hydrazone. It has been found also by one of us that when *iso*nitrosocamphor, the monoxime of camphorquinone, is treated with hydrazine hydrate, the change is similar to that incurred by benzil-α-monoxime, the product being camphorquinonehydrazone instead of the hydrazoxime. The fact that the *syn*-configuration has been assigned to both benzil-α-monoxime and to the stable form of *iso*nitrosocamphor, appears to us significant, suggesting that the attack of the hydrazine on the free carbonyl group is hindered by the propinquity of the hydroxyl radicle; the actual change is probably analogous to that which takes place when hydroxylamine acetate acts on derivatives of phenyliminocamphor (Trans., 1909, **95**, 942), this having been shown to involve the formation of an additive compound, from which the removal of amine leads to *iso*nitrosocamphor. In the case under discussion, the intermediate additive compound must lose hydroxylamine, thus yielding the hydrazone instead of the oxime:



$$\begin{array}{l}C_6H_5\cdot C{:}NOH\\ \quad|\\ C_6H_5\cdot CO\end{array} \xrightarrow{N_2H_4} \begin{array}{l}C_6H_5\cdot C<\begin{array}{l}NH\cdot OH\\ NH\cdot NH_2\end{array}\\ \quad|\\ C_6H_5\cdot CO\end{array} \longrightarrow \begin{array}{l}C_6H_5\cdot C{:}N\cdot NH_2\\ \quad|\\ C_6H_5\cdot CO\end{array} + NH_2\cdot OH.$$

When hydrazine hydrate acts on benzil-β-monoxime, however, the oximino-group is not disturbed, and the hydrazoxime,

$$C_6H_5\cdot C({:}NOH)\cdot C({:}N\cdot NH_2)\cdot C_6H_5,$$

is produced. This readily undergoes condensation with acetone or benzaldehyde, and yields a monoformyl and monobenzoyl derivative, whilst a diacetyl derivative is formed with acetic anhydride. Although these changes are normal, the action of mineral acids does not follow the usual course, namely, removal of hydrazine (1 mol.) from two molecular proportions of the substance; the expected azine was not produced either by this method or by condensation of the hydrazoxime with benzilmonoxime.

In connexion with the difference in behaviour towards hydrazine hydrate displayed by the two monoximes of benzil, it should be noted that Auwers and Siegfried (*Ber.*, 1892, **25**, 2597; see also 1893, **26**, 788) found that whilst the same anil is furnished by both oximes, the α-oxime is the only one which yields a phenylhydrazone; thus, in behaviour towards benzil, hydrazine appears to be the converse of phenylhydrazine; but, on the other hand, it must be pointed out that separate phenylhydrazones are obtained from the two forms of *iso*nitrosocamphor, so that it is impossible at this stage to attempt any useful generalisation concerning these agents.

There is no great disparity between the hydrazoxime just described and that of diacetyl. As in the former case, condensation of the hydrazine residue takes place with acetone or benzaldehyde, whilst acetic anhydride forms a diacetyl derivative, although the product from benzoyl chloride contains only one acyl group, this compound being more conveniently obtained by condensation between diacetylmonoxime and benzoylhydrazine, thus defining the position of the benzoyl group. The corresponding azine, however, can be produced very readily from diacetylhydrazoxime,

$$2[CH_3\cdot C(\colon NOH)\cdot C(CH_3)\colon N\cdot NH_2] = NH_2\cdot NH_2 + [CH_3\cdot C(\colon NOH)\cdot C(CH_3)\colon N]_2;$$

so readily, indeed, does this change take place under the influence of acids that even exposure to air causes the colourless hydrazoxime to become superficially yellow in the course of a few days.

In conclusion, it should be noted that although, in distinction from the benzilmonoximes, benzilhydrazoxime forms a colourless solution in aqueous alkalis, the acyl derivatives resemble the oximes themselves in developing a yellow coloration on dissolution. This colour must be ascribed to the acylated hydrazine residue, and is independent of the oximino-group because it persists when the latter is acylated. It is therefore to be classified with the colour developed by the monosemicarbazones of α-diketones, first noticed by Diels (*Ber.*, 1902, **35**, 347; see also Diels and vom Dorp, *Ber.*, 1903, **36**, 3183; Forster and Zimmerli, Trans., 1910, **97**, 2156). In view of the fact that the phenomenon is restricted to acylated hydrazine derivatives, to which, therefore, the group $\colon N\cdot NH\cdot CO\cdot X$ is common, and is not displayed by the corresponding phenylhydrazones, it may be argued that the development of colour depends on salt formation following the change:

$$\colon N\cdot NH\cdot CO\cdot X \longrightarrow \colon N\cdot N\colon C(OH)X.$$

Whence it appears that the effect of the oximino-group (free or acylated) is the same as that of the free carbonyl group in the monosemicarbazones of α-diketones.

EXPERIMENTAL.

Benzilhydrazoxime, $C_6H_5 \cdot C(\colon NOH) \cdot C(\colon N \cdot NH_2) \cdot C_5H_5$.

Fifteen grams of benzil-β-monoxime dissolved in 50 c.c. of alcohol were heated with 8 grams of 60 per cent. hydrazine hydrate under reflux during four hours, a small proportion of water being then added; the crystalline deposit weighed 12 grams, and when recrystallised from hot alcohol separated in hard, transparent plates melting at 170°, slowly liberating gas on further heating:

0·1265 gave 0·3269 CO_2 and 0·0643 H_2O. C = 70·48; H = 5·65.
0·2574 „ 39·5 c.c. N_2 at 24° and 755 mm. N = 17·59.
$C_{14}H_{13}ON_3$ requires C = 70·29; H = 5·44; N = 17·57 per cent.

The hydrazoxime is readily soluble in alcohol, acetone, or ether, but dissolves less freely in hot chloroform, of which it requires about eight parts; benzene dissolves it very sparingly, and it is insoluble in petroleum. It rapidly develops a mirror with ammoniacal silver oxide, but is without action on Fehling's solution. Aqueous alkali hydroxide forms a colourless solution, from which acids precipitate unchanged material, whilst ferrous sulphate fails to give a characteristic coloration; the alcoholic solution is indifferent towards ferric chloride. When suspended in cold hydrochloric acid the hydrazoxime immediately becomes faint yellow, but on recrystallising the product from alcohol only unaltered substance is recovered; moreover, no definite change can be recognised when nitrous acid acts on it, although in other cases this treatment leads to the azine.

The *formyl* derivative, prepared by gently warming the hydrazoxime with formic acid (D 1·2), separated from warm dilute alcohol in somewhat indefinite crystals melting at 211°:

0·1471 gave 20·5 c.c. N_2 at 24° and 753 mm. N = 15·92.
$C_{15}H_{13}O_2N_3$ requires N = 15·73 per cent.

It is insoluble in water, benzene, or petroleum, but dissolves in ether or chloroform. There is not any reduction of ammoniacal silver oxide or Fehling's solution, and the yellow liquid produced on dissolving the substance in cold aqueous alkali yields it unchanged on acidification.

The *diacetyl* derivative, although formed when the hydrazoxime is dissolved in glacial acetic acid, is more conveniently obtained with acetic anhydride, and separates from alcohol in stellate aggregates of hard, prismatic needles, melting at 170°:

0·1498 gave 17·3 c.c. N_2 at 21° and 763 mm. N = 13·13.
$C_{18}H_{17}O_3N_3$ requires N = 13·01 per cent.

It is moderately soluble in hot alcohol, chloroform, or benzene, but is insoluble in ether, and it does not reduce ammoniacal silver oxide or Fehling's solution. Warm aqueous alkali forms a yellow solution.

The *benzoyl* derivative, prepared from an alcoholic solution and benzoyl chloride, is very sparingly soluble in all ordinary media, such as alcohol, benzene, chloroform, or petroleum, and is best recrystallised by adding a small proportion of water to a solution in pyridine. It becomes yellow at 227°, and melts and decomposes at 231°:

0·0891 gave 0·2397 CO_2 and 0·0412 H_2O. C=73·36; H=5·11.
0·1374 ,, 15·6 c.c. N_2 at 24° and 753 mm. N=12·96.
$C_{21}H_{17}O_2N_3$ requires C=73·46; H=4·95; N=12·25 per cent.

It resembles the foregoing acyl derivatives in forming a yellow solution in aqueous alkali when warmed, and then yields a rose-coloured precipitate with ferrous sulphate.

The *acetone* derivative is formed on boiling a solution of the hydrazoxime in the ketone, and crystallises from dilute alcohol in pale yellow, prismatic needles, melting at 150·5°:

0·1324 gave 17·7 c.c. N_2 at 21° and 750 mm. N=15·36.
$C_{17}H_{17}ON_3$ requires N=15·05 per cent.

The substance dissolves readily in organic media excepting benzene, in which it is only sparingly soluble; there is not any reduction of ammoniacal silver oxide, and it is insoluble in aqueous alkali.

The *benzylidene* derivative crystallises from alcohol in stellate groups of soft, yellow needles, melting and decomposing at 202°:

0·1577 gave 17·6 c.c. N_2 at 20° and 750 mm. N=12·87.
$C_{21}H_{17}ON_3$ requires N=12·84 per cent.

It is moderately soluble in alcohol, ether, chloroform, or acetone, but is insoluble in petroleum. Glacial acetic acid hydrolyses the substance, which is not dissolved by aqueous alkali.

Diacetylhydrazoxime, $CH_3\cdot C(:NOH)\cdot C(:N\cdot NH_2)\cdot CH_3$.

On adding hydrazine hydrate to an alcoholic solution of diacetylmonoxime, the liquid became warm and deep yellow, the colour fading with lapse of time; after twenty-four hours the crystalline deposit, weighing 9 grams from 10 grams of the oxime, consisted principally of colourless needles with a few nodules. When extracted with boiling benzene, of which about 40 c.c. was required by 1 gram, the solvent deposited snow-white, silky needles mixed with hard prisms, the melting point of the mixture being indefinite; it has not been possible to isolate the former modification, because recrystallisation appears to convert the needles into the prisms, which melt at 140°:

0·1428 gave 0·2152 CO_2 and 0·1082 H_2O. C=41·11; H=8·42.
0·1140 „ 36·5 c.c. N_2 at 20° and 744 mm. N=36·61.
$C_4H_9ON_3$ requires C=41·74; H=7·82; N=36·52 per cent.

The hydrazoxime is soluble in cold water, and reduces ammoniacal silver oxide and Fehling's solutions; ferric chloride develops an intense, blood-red coloration, which is destroyed by mineral acid. Alcohol dissolves it freely, but it is less readily soluble in ether, and sparingly so in benzene or chloroform, both of which are convenient media for recrystallisation. The solution in aqueous alkali is colourless.

Although the substance begins to decompose when heated above the melting point, a considerable proportion undergoes sublimation, the nitrogen and ammonia which are set free by the chemical change carrying the vapour into cooler parts of the tube, where long, glistening needles, melting at the same temperature as the pure substance, are deposited. No definite product was separated from the residue, but in view of the yellow colour and the facility with which the azine is produced (see below), this material is doubtless present.

The *diacetyl* derivative, prepared with warm acetic anhydride, was crystallised from alcohol, forming snow-white needles melting at 182°:

0·0715 gave 13·6 c.c. N_2 at 21° and 746 mm. N=21·78.
$C_8H_{13}O_3N_3$ requires N=21·11 per cent.

It dissolves freely in organic media excepting benzene, in which it is only sparingly soluble; hot water also dissolves it, and its reducing power is very slight. The solution in aqueous sodium hydroxide is colourless.

The *benzoyl* derivative, obtained by mixing aqueous solutions of diacetylmonoxime and benzoylhydrazine, was recrystallised from hot alcohol, forming stellate clusters:

0·1238 gave 21·3 c.c. N_2 at 21° and 747 mm. N=19·61.
$C_{11}H_{13}O_2N_3$ requires N=19·18 per cent.

The substance melts at 201°, dissolves readily in alcohol or acetone, more sparingly in ether or chloroform, and is insoluble in benzene or petroleum. It does not reduce ammoniacal silver oxide, and the solution in aqueous alkali is faint yellow, forming an intense Prussian-blue coloration with ferrous sulphate.

The *acetone* derivative was produced on attempting to recrystallise the hydrazoxime from warm acetone, in which it is freely soluble:

0·0984 gave 23·7 c.c. N_2 at 24° and 748 mm. N = 27·37.
$C_7H_{13}ON_3$ requires N = 27·10 per cent.

The substance crystallises in long, silky needles, melting at 110°; if it is allowed to remain in the mother liquor, bubbles appear, and the liquid becomes yellow, depositing the azine on spontaneous evaporation. The same change occurs in the dry material when exposed to air.

On attempting to prepare the *benzylidene* derivative by warming the factors in ethyl alcohol, the liquid became bright yellow, and in the course of twelve hours deposited benzalazine, melting at 96°. The required substance was obtained, however, by adding 4 grams of benzaldehyde to a solution containing 4·5 grams of the hydrazoxime in 30 c.c. of methyl alcohol, warming to 40—50°, diluting until turbid, and recrystallising the pale yellow product from alcohol:

0·0693 gave 12·6 c.c. N_2 at 24° and 748 mm. N = 20·65.
$C_{11}H_{13}ON_3$ requires N = 20·68 per cent.

The substance melts at 107°, resembling the corresponding derivative of benzilhydrazoxime in appearance and solubilities.

The Azine of Diacetylmonoxime, $[CH_3\cdot C(:NOH)\cdot C(CH_3):N]_2$.

Under the influence of acids, the hydrazoxime readily parts with hydrazine, even glacial acetic acid producing this change if gently warmed. When covered with cold hydrochloric acid, the colourless hydrazoxime immediately becomes yellow, afterwards changing to a white, crystalline powder consisting of hydrazine hydrochloride. Three convenient methods for the preparation of the azine have been found, namely, agitation with 5 per cent. hydrochloric acid, treatment of the hydrazoxime in acetic acid with sodium nitrite, and condensation of diacetylmonoxime itself with the hydrazoxime, the last-named process taking place quantitatively when the factors are mixed in aqueous solution:

0·0560 gave 13·9 c.c. N_2 at 24° and 755 mm. N = 28·42.
$C_8H_{14}O_2N_4$ requires N = 28·28 per cent.

The compound is insoluble in petroleum, and dissolves very sparingly in other media, even when these are boiled; it dissolves more readily in pyridine or ether, a mixture of alcohol and ether being the most convenient from which to crystallise it, although the crystals are small and indefinite. It melts and decomposes at 230°, becoming darker yellow at a few degrees below this temperature.

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CCXXXIV.—*The Oxidation of Aconitine.*

By Francis Howard Carr.

Although we have a fairly complete knowledge of the simpler groups contained in the aconitine molecule, nothing is known regarding the main features of its constitution. From the work of Dunstan, Freund, Schulze, and their collaborators it may be inferred that aconitine, $C_{34}H_{47}O_{11}N$, contains the following groups: one acetyl, benzoyl and *N*-methyl, four methoxyl, and three hydroxyl groups, and may therefore be represented as derived from a hypothetical base, $C_{20}H_{31}N$, thus:

$$C_{20}H_{21}N\begin{cases}CH_3\\(OH)_3\\OAc\\OBz\\(OMe)_4\end{cases}.$$

Hitherto, however, although Schulze (*Arch. Pharm.*, 1906, **244**, 165) made experiments on the oxidation, no suitable means of attack has been proposed whereby the constitution of this hypothetical base may become elucidated. The compound obtained by the oxidation of aconitine, which is described in the present paper, appears likely to overcome this difficulty in some measure.

In a paper describing aconitine permanganate, $C_{34}H_{47}O_{11}N,HMnO_4$, Dunstan and Carr (*Pharm. J.*, 1896, [iv], 2, 122) pointed out that by the spontaneous decomposition of this salt there was derived from aconitine a new oxidation product, the further investigation of which was in progress. This research, which had led to some important results, was interrupted in 1897 owing to the present author's removal to a new position. It was intended to resume the investigation later, but only now, after fifteen years have elapsed, has an opportunity of doing so arisen. Dr. G. Barger is collaborating in the continuation of the work; meanwhile it is thought best to publish at the present stage the results already obtained.

When aconitine permanganate in the presence of dilute sulphuric acid is allowed to remain at the room temperature for several days, or for a less time if the action be accelerated by raising the temperature to 40°, a neutral white, crystalline substance results, together with one molecular proportion of acetaldehyde.

For this neutral substance, the name *oxonitin* is proposed. It has the empirical formula $C_{23}H_{29}O_9N$.

The oxidation of aconine, a base derived from aconitine by hydrolysis, was studied by Schulze (*loc. cit.*) many years after the experiments here described were carried out. He observed the formation of acetaldehyde when alkaline permanganate or chromic acid is employed.

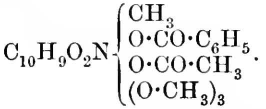
In the latter case methylamine and a substance both acid and basic were formed, also a new base, $C_{24}H_{35}O_3N$, derived from aconine according to the following equation :

$$C_{25}H_{41}O_9N + 2O_2 = CO_2 + 3H_2O + C_{24}H_{35}O_8N.$$

Schulze, however, did not obtain a substance similar to oxonitin or its hydrolytic products.

Oxonitin crystallises from a mixture of chloroform and methyl alcohol in white, prismatic needles, melting at 276—277°, and decomposing at this temperature with the evolution of acetic acid. It has $[\alpha]_D$ −62° in chloroform. It is sparingly soluble in all solvents that have been tried. Ether, benzene, water or dilute acids fail to dissolve it, whilst its solubility in chloroform, in absolute acetic acid, and in pyridine is only slight; but it is more readily dissolved by phenol or fuming hydrochloric acid. From the latter solvent, oxonitin may be recovered unchanged by dilution with water, a circumstance which affords a useful method of purification. Oxonitin is tasteless, is neutral in reaction, does not combine with acids or alkalis, and does not give a precipitate with the common alkaloidal reagents.

Oxonitin is a saturated substance, unaffected by bromine, iodine, or sodium amalgam. Methyl iodide, hydroxylamine, and acetic anhydride fail to act on it. It contains three methoxyl groups, and since it gives, like aconitine, both acetic and benzoic acids on hydrolysis, it contains also an acetyl and benzoyl group. It may be presumed that the *N*-CH_3 group contained in aconitine is unchanged; its constitution may therefore be represented thus :



$$C_{10}H_9O_2N\begin{cases} CH_3 \\ O{\cdot}CO{\cdot}C_6H_5 \\ O{\cdot}CO{\cdot}CH_3 \\ (O{\cdot}CH_3)_3 \end{cases}.$$

This substance differs from aconitine by $C_{10}H_{14}(OH)(OCH_3)$, the fate of most of which is still unknown. One molecular proportion of permanganate is required for the change, less than this resulting in unchanged aconitine, and the full amount giving under proper conditions a theoretical yield. Two and a-half atomic proportions of oxygen are therefore concerned in the change.

If the permanganate is allowed to blacken in the air, no gas or volatile product is formed. When the blackened precipitate is dissolved in dilute sulphuric acid, one molecular proportion of acetaldehyde is produced, but no gas is evolved. If, however, a further quantity of permanganate is added to the mixture which has already reacted, two molecular proportions of carbon dioxide are evolved. It is thought that this points to the probable presence of oxalic acid among the oxidation products. No volatile acid is produced, but an intractable amorphous residue remains.

In the continuation of the work endeavour will be made to elucidate the constitution of the parent base, $C_{10}H_{15}O_2N$.

Japaconitine, $C_{34}H_{49}O_{11}N$, which differs only from aconitine in containing two more hydrogen atoms, yielded oxonitin when oxidised by the same method, identified by the determination of $[\alpha]_D$ and the melting point. Pseudaconitine, $C_{36}H_{51}O_{12}N$, which contains a veratryl group, on the other hand does not yield oxonitin; but aldehyde is formed, and a substance crystallising in large, irregular plates melting at 235°, which has not been further investigated.

Oxonitin affords different products according as the hydrolysis is brought about by alkali or by hydrochloric acid.

When hydrolysed with alcoholic sodium hydroxide at 80—90°, molecular proportions of acetic and benzoic acids are split off from oxonitin; but in this case a neutral substance containing, nitrogen, and not an alkaloid, is produced. This may be extracted with chloroform and crystallised from a mixture of alcohol, ether, and petroleum in spherical nodules melting at 82°. It is readily soluble in water, is neutral to litmus, and gives no reaction with Mayer's reagent.

On hydrolysis with boiling hydrochloric acid, acetic and benzoic acids are split off from oxonitin, and an alkaloid soluble in ether remains, which crystallises from alcohol and melts at 265°. The hydrochloride, hydrobromide, and aurichloride were prepared, but could not be crystallised from water, alcohol, or anhydrous solvents, although a few crystals of the hydrobromide were obtained from benzene and from absolute alcohol. The picrate is insoluble and amorphous. The base reduces potassium permanganate. Negative results were obtained with Gaebel's test (*Arch. Pharm.*, 1910, **248**, 226) for methylenedioxy-groups. It also failed to give the pine-shaving test for pyrroles. Hitherto this alkaloid has been obtained in quantities insufficient for analysis.

If this substance is derived by the replacement of acetyl and benzoyl groups by hydrogen, its formula may be written $C_{11}H_{14}O_4N(OCH_3)_3$. In any case it affords a promising opportunity of gaining important information regarding the constitution of aconitine.

EXPERIMENTAL.

Oxonitin is produced only when the oxidation of aconitine by permanganate is carried out in a particular manner. The yield is apt to be very low unless attention is paid to details.

Preparation of Aconitine Permanganate.

A neutral solution of aconitine sulphate cooled to 0° is precipitated by the cautious addition of cold potassium permanganate solution; the insoluble permanganate, as soon as the precipitation is complete, being filtered under pressure in an ice-jacketed funnel and washed with ice-cold water.

Aconitine permanganate is a red substance which is seen under the microscope to consist of rosettes of prismatic, short, stout crystals. It is sparingly soluble in water—about 1 in 5000—and readily soluble in glacial acetic acid. If left in the air at the ordinary temperature, in or out of the light, it slowly blackens and gives off acetaldehyde:

0·4068 gave 0·0423 Mn_3O_4. Mn = 7·48.

$C_{34}H_{47}O_{11}N,HMnO_4$ requires Mn = 7·29 per cent.

Preparation of Oxonitin.

Freshly precipitated aconitine permanganate is dried in a vacuous desiccator, when it blackens; it is then kept at 40° for several days in contact with 15 per cent. sulphuric acid, using about 1 c.c. to each gram of aconitine taken. After the last traces of brown oxide of manganese have disappeared, the white, insoluble, crystalline substance remaining is collected, dried, and purified by recrystallisation. The maximum yield obtained was 68 per cent. of the weight of aconitine taken, representing 95 per cent. of the theoretical yield, although it usually falls lower than this figure. Other conditions than those mentioned were found to give lower yields, in some cases as little as 15 per cent.

Very many other methods of oxidation were tried unsuccessfully; for instance, direct oxidation with excess of permanganate, oxidation with manganese dioxide and sulphuric acid, permanganate in alkaline solution, chromic acid and hydrogen peroxide.

Oxonitin may best be purified by dissolving in fuming cold hydrochloric acid and crystallising by the addition of water. It may then be recrystallised by dissolving it in a mixture of two parts of chloroform and one part of methyl alcohol, and adding dry ether. No other solvent was found from which it can be suitably crystallised.

A study of the condition under which aconitine is oxidised to oxonitin showed that the whole of the available oxygen from an equimolecular proportion of potassium permanganate is used up ($2\frac{1}{2}$ atomic proportions). No oxygen is evolved during the action of sulphuric acid on the precipitated permanganate, and unchanged aconitine may be recovered during the intermediate stages.

In order to determine the quantity and nature of the gases evolved during the oxidation, an experiment was conducted in a nitrometer. The freshly precipitated permanganate from 0·4014 gram of aconitine was acted on by 10 per cent. sulphuric acid at 50° over mercury; the amount of gas evolved measured only 0·7 c.c. On introducing an excess of permanganate, a rapid evolution of gas took place, 28 c.c. being evolved.

Analysis showed the gas to contain 27·7 c.c. of carbon dioxide and 0·3 c.c. of oxygen, whilst the calculated amount for 2 molecular proportions of carbon dioxide from aconitine is 27·8 c.c.

The oxidation appears to occur in two stages: the first in which the permanganate darkens, during which no aldehyde is produced, and the second, due to the action of the sulphuric acid on the darkened precipitate, when acetaldehyde is produced. The identity of the aldehyde was shown by oxidising the neutral distillate with chromic acid and analysing the silver salt of the acid thus formed. (Found, Ag = 64·1. Calc., Ag = 64·6 per cent.)

The amount of aldehyde produced was estimated by the following method. The aconitine was dissolved in dilute sulphuric acid to exact neutrality, cooled to 0°, and precipitated with a cold solution of potassium permanganate. The precipitate was collected on a funnel jacketed above and around with ice, and was transferred to a distilling flask and there allowed to darken; dilute sulphuric acid was then introduced, and the aldehyde distilled off into a flask, containing silver oxide suspended in water, and fitted with a reflux condenser. The silver solution was gently warmed, and the excess of oxide removed from the reduced silver by washing with ammonia. The silver was then dissolved in nitric acid and precipitated, and weighed as chloride in the usual manner. (Found, 0·280 gave 0·1294 AgCl. Ag = 34·7. Calc. for one molecular proportion of $CH_3·COH$, Ag = 33·3 per cent.)

Properties of Oxonitin.

Oxonitin crystallises in rosettes of white, prismatic crystals. When placed in the bath at 240° it melts, and decomposes at 276—277° It is sparingly soluble in alcohol, chloroform, phenol, pyridine or glacial acetic acid, insoluble in ether, benzene, water or dilute acids.

Solubility.—(1) In chloroform:

18 c.c. saturated at 15° gave 0·1403 gram, or 100 c.c. dissolve 0·78 gram.

(2) In absolute acetic acid:

15·9 c.c. saturated at 12° gave 0·0771 gram, or 100 c.c. dissolve 0·48 gram.

(3) In pyridine:

1·0 c.c. saturated at room temperature gave by evaporation 0·017 gram, or 100 c.c. dissolve 1·7 grams.

Oxonitin is neutral in reaction, does not combine with acids or with alkalis, and does not give precipitates with Mayer's reagent or phosphotungstic acid.

0·1017, dissolved in dry chloroform and made up to 20 c.c., gave in a 2-dcm. tube at 160°, a_D $-0{\cdot}63°$, whence $[a]_D$ $-62°$:

0·3400 gave 0·7409 CO_2 and 0·2004 H_2O. C = 59·43; H = 6·55.
0·2603 „ 0·5666 CO_2 „ 0·1527 H_2O. C = 59·36; H = 6·52.
0·2442 „ 0·5287 CO_2 „ 0·1370 H_2O. C = 59·04; H = 6·23.
0·2635* required 6·08 c.c. *N*/10-acid. N = 3·19 per cent.

0·2951 gave 8·2 c.c. N_2 at 18° and 752 mm. N = 3·2.
0·1931 „ 0·2834 AgI. OMe = 19·35.
0·1630 „ 0·2382 AgI. OMe = 19·27.
$C_{23}H_{29}O_9N$ requires C = 59·6; H = 6·26; N = 3·04; 3MeO = 20·1 per cent.

The molecular weight was determined by the cryoscopic method in phenol:

0·5090 in 16·14 gave $\Delta t = -0{\cdot}500°$. M.W. = 473.

A determination was made by the microscopic method by Dr. G. Barger, to whom the author wishes to record his thanks:

0·017 in 0·9782 pyridine was about 0·04 mol. M.W. = 434.
$C_{23}H_{29}O_9N$ requires M.W. = 463.

Iodine in chloroform solution was allowed to act on oxonitin for twenty-hours, but the latter was recovered unchanged. Bromine in the same way failed to combine. Sodium amalgam does not act on it either in alcohol or in water; it is therefore a saturated compound.

Acetic anhydride in large excess in chloroform did not act on it even when heated, the oxonitin being nearly all recovered unchanged.

Acetic anhydride and anhydrous sodium acetate similarly failed to act on it.

Acetyl chloride in chloroform acts on it, forming a colourless, amorphous varnish sparingly soluble in water, readily so in chloroform, alcohol, ethyl acetate, or acetic acid, and less readily so in ether or carbon tetrachloride. All efforts to crystallise this substance were unavailing. It seems probable that it is a derivative of the product which results from the action of hydrochloric acid on oxonitin and not an acetyl derivative of oxonitin.

The two oxygen atoms which remain unaccounted for therefore appear not to be hydroxylic; nor are they ketonic, for hydroxylamine dissolved in methyl alcohol has no action on oxonitin, the substance being recovered unchanged.

When an excess of methyl iodide was heated with oxonitin in methyl alcohol at 100—110°, the oxonitin was recovered unchanged.

Glacial acetic acid at 100° and 18 per cent. ammonia solution at 120° were without action on it.

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* By Will and Varrentrapp's method.

When heated in a dry condition at its melting point, oxonitin gives off acetic acid (0·2266 gave 0·0201 acetic acid = 8·9 per cent.)

Since the acetyl group of aconitine may be replaced by methyl by heating the base with methyl alcohol, it was thought likely that the same change could be effected on oxonitin; but even after heating to 160—180° in a sealed tube for five hours most of the substance was recovered from the methyl alcohol unchanged. An odour of methyl benzoate, however, was observed, and the mother liquors contained a small amount of an alkaloid.

Hydrolysis.

Oxonitin undergoes hydrolysis when heated with water at 150° in a sealed tube or with ammonia at 135°, but the hydrolysis is best brought about by heating with alcoholic sodium hydroxide.

Weighed quantities of oxonitin were dissolved in pure absolute alcohol, a solution of pure sodium hydroxide prepared from sodium was added, and the whole heated on the water-bath for two hours at 80—90°. The alcohol was then evaporated, and the aqueous alkaline liquid repeatedly extracted with benzene; in this way hydrolytic products except acetic acid were removed, the latter being estimated by distilling into *N*/10-alkali. The benzoic acid contained in the acid benzene extract was then shaken into *N*/10-alkali and titrated:

0·5048 gave acetic acid requiring 10·7 c.c. *N*/10-NaOH = 12·7 per cent. acetic acid.

1·1097 gave acetic acid requiring 23·7 c.c. *N*/10-NaOH = 12·8 per cent. acetic acid.

1·0781 gave benzoic acid requiring 19 c.c. *N*/10-NaOH = 21·4 per cent. benzoic acid.

$C_{23}H_{29}O_9N$ requires for one molecule $C_2H_4O_2 = 12·9$ per cent.

$C_{23}H_{29}O_9N$,, ,, ,, $C_7H_6O_2 = 26·3$,, ,,

The acetic acid was identified by the analysis of its silver salt (Found, Ag = 64·15. Calc., Ag = 64·6 per cent.), and the benzoic acid by its appearance and melting point (122°). Traces of butyric and formic acids were apparently present among the hydrolytic products.

The other product of hydrolysis which may be extracted from the alkaline solution with benzene or chloroform is a neutral substance containing nitrogen. This was crystallised with much difficulty from a mixture of alcohol, ether, and petroleum in spherical nodules melting at 82°. It is tasteless, readily soluble in water, and neutral to litmus. It gives no reaction with Mayer's reagent. Insufficient was obtained in a crystalline form to permit of analysis.

The Action of Hydrochloric Acid.

If a solution of oxonitin in fuming hydrochloric acid is boiled under reflux, a change takes place resulting in the formation of an alkaloid. This change is partly of the nature of hydrolysis, acetic and benzoic acids being produced. Owing to the difficulty of determining acetic acid in the presence of hydrochloric acid, the amount produced has not been determined, but the amount of benzoic acid corresponds with one molecular proportion :

0·2391 gave 0·0701 $C_7H_6O_2 = 25·1$.

$C_{23}H_{29}O_9N$ requires $C_7H_6O_2 = 26·3$ per cent.

In an experiment, 0·25 gram of oxonitin was heated with fuming hydrochloric acid at 100° in a sealed tube for one hour. The tube was cooled at 0° and opened while connected to a gas burette, when it was found that no gas was evolved. The temperature was raised to 50°, and still no gas was driven off except hydrochloric acid. Hence no methyl chloride was produced, and the methoxyl groups may be presumed to remain intact.

The alkaloid resulting from this treatment, which has only been produced in small amount, is colourless, insoluble in water, and soluble in ether, chloroform, alcohol, light petroleum, benzene, etc. It crystallises readily from mixtures of alcohol and ether, and melts and decomposes at 265°.

The salts are crystallisable with very great difficulty, and a few crystals of both the hydrochloride and hydrobromide were ultimately formed from absolute alcohol. Fifteen different solvents and mixed solvents were employed in efforts to find a suitable method of purifying them, but proved unsuccessful.

The aurichloride was deposited as a canary-yellow precipitate by the addition of gold chloride to an aqueous solution of the hydrochloride, but it could not be crystallised. On the addition of dry ether to an alcoholic solution a colourless gold salt was precipitated.

In conclusion, the author wishes to acknowledge his indebtedness to Prof. Wyndham R. Dunstan, at whose instance the work was conducted; and to the authorities of the Pharmaceutical Society and of the Imperial Institute, in whose laboratories the research was for the greater part conducted.

CCXXXV.—*Electromotive Forces in Alcohol. Part III. Further Experiments with the Hydrogen Electrode in Dry and Moist Alcoholic Hydrogen Chloride.*

By Robert Taylor Hardman and Arthur Lapworth.

It was shown in Part II. (Trans., 1911, **99**, 2242 *et seq.*) that the influence of water on the electromotive force of the hydrogen electrode in alcoholic hydrogen chloride at 25° is of the nature required by the solvate theory of acids, the quantitative results at this temperature being in very fairly satisfactory agreement with the relative affinity values of water and alcohol previously deduced by two purely chemical methods.

The work described in the present paper is an extension of that described in Part II., and with special reference to (i) the electromotive forces of hydrogen ion concentration cells with solutions of hydrogen chloride in absolute alcohol as cell liquids, and (ii) the influence of temperature on the intensity of the disturbance produced in such cells by addition of water.

Electromotive Forces of Hydrogen Ion Concentration Cells with Absolute Alcoholic Hydrogen Chloride as Cell Liquid.

It was previously shown that the transport number of the chloridion in alcoholic hydrogen chloride, as deduced by the application of Nernst's formula to results of transport measurements with concentration cells with electrodes reversible to chloridion, was very much higher than that for chloridion in the aqueous acid, namely, about 0·37, as contrasted with 0·167 (Trans., 1911, **99**, 1418 *et seq.*). Preliminary experiments with the hydrogen electrode, on the other hand, led to results suggesting a transport number varying considerably with the concentration of the acid, and usually lower than that previously inferred from other considerations (compare Trans., 1911, **99**, 2246 *et seq.*).

A careful series of measurements with such cells, reversible to hydrogen ions, with absolute alcohol as cell liquid, has therefore been undertaken, every precaution which suggested itself having been observed to ensure and maintain the purity of the agents and vessels used. The electromotive force of each combination was determined at least three times with solutions prepared from different samples of alcohol, and only those results are included in the following tabulation which satisfied all the criteria of trustworthiness which we have found applicable for results with these combinations, namely, (*a*) rapid attainment of final *E.M.F.*;

(*b*) sharpness and constancy of final *E.M.F.* over considerable periods; (*c*) rapid reproduction of the same *E.M.F.* on changing the electrodes or cell-liquids.

The apparatus used was identical with that used for the measurements in Part II., except that the slide-wire bridge was replaced by a potentiometer made by the Land- und Seekabelwerke, very carefully calibrated, and capable of being read with accuracy to less than 0·0001 volt.

As before, the temperature was 25° ± 0·05.

The arrows, as usual, represent the direction of the positive current inside the cells.

$$\text{(1)}\quad H_2,1{\cdot}0N\text{-HCl}\,\underset{\longleftarrow}{|}\,0{\cdot}3162N\text{HCl},H_2.$$

Number of combinations included = 4.

Extreme variation of *E.M.F.* in the four cells = 0·2 millivolt. Mean *E.M.F.* = 0·0139 volt.

$$\text{(2)}\quad H_2,0{\cdot}3162N\text{-HCl}\,\underset{\longleftarrow}{|}\,0{\cdot}1N\text{-HCl},H_2.$$

Number of combinations included = 3.

Extreme variation of *E.M.F.* in the three cells = 0·2 millivolt. Mean *E.M.F.* = 0·0108 volt.

$$\text{(3)}\quad H_2,1{\cdot}0N\text{-HCl}\,\underset{\longleftarrow}{|}\,0{\cdot}1N\text{-HCl},H_2.$$

Number of combinations included = 9.

Extreme variation of *E.M.F.* in nine cells = 3·5 millivolts.

” ” ” rejecting three most discordant values = 0·7 millivolt.

Mean *E.M.F.* = 0·0256 volt.

$$\text{(4)}\quad H_2,0{\cdot}10N\text{-HCl}\,\underset{\longleftarrow}{|}\,0{\cdot}03162N\text{-HCl},H_2.$$

Number of combinations included = 3.

Extreme variation in *E.M.F.* in 3 combinations = 0·4 millivolt. Mean *E.M.F.* = 0·0108 volts.

$$\text{(5)}\quad H_2,0{\cdot}03162N\text{-HCl}\,\underset{\longleftarrow}{|}\,0{\cdot}01N\text{-HCl},H_2.$$

Number of combinations included = 3.

Extreme variation of *E.M.F.* in three combinations = 0·4 millivolt. Mean *E.M.F.* = 0·0107 volt.

$$\text{(6)}\quad H_2,0{\cdot}1N\text{-HCl}\,\underset{\longleftarrow}{|}\,0{\cdot}01N\text{-HCl},H_2.$$

Number of combinations included = 8.

Extreme variations of *E.M.F.* in 8 cells = 1·5 millivolts. Mean *E.M.F.* = 0·0233 volt.

The "probable error" in the series (3) and (6) was about 0·2 millivolt, and in the other instances was less than 0·1 millivolt.

From these data transport numbers for chloridion have been calculated in each instance with the aid of the formula:

$$E = 2(1 - n)\frac{RT}{F}\log\frac{\lambda_1 c_1}{\lambda_2 c_2},$$

where the symbols used have their usual significance. The values for λ, the molecular conductivity, were determined by interpolation, with reference to the known concentrations of hydrochloric acid, from measurements of conductivity previously recorded (Trans., 1911, **99**, 1425). No correction was made for viscosity differences.

The values for the transport number for chloridion in alcoholic hydrogen chloride are given in the following table, which summarises all the foregoing results.

Here c_1 and c_2 represent the total volume-molecular concentrations of hydrogen chloride used in each of six combinations, E is mean electromotive force observed, and $(1 - n)$ is the transport number for chloridion deduced as above:

Series.	c_1.	c_2.	E (volts).	$1 - n$.
1.	N	$N/\sqrt{10}$	0·0139	(0·35)
2.	$N/\sqrt{10}$	$N/10$	0·0108	(0·25)
3.	N	$N/10$	0·0256	0·30
4.	$N/10$	$N/10 \times \sqrt{10}$	0·0108	(0·22)
5.	$N/10 \times \sqrt{10}$	$N/100$	0·0107	(0·21)
6.	$N/10$	$N/100$	0·0233	0·25

It may be noted that E in series 3 should theoretically be identical with the sum of E_1 and E_2, whilst in point of fact there is a discrepancy of 0·9 millivolt. Similarly, E_6 differs from $E_4 + E_5$ by 1·8 millivolts.

The deduced values of $1 - n$ thus appear to diminish considerably on passing from concentrated to dilute solutions (compare Trans., 1911, **99**, 2249 *et seq.*). The maximum value in the present instance is in close agreement with the number deduced from observations with cells reversible to chloridions, as well as from other considerations (Trans., 1911, **99**, 1420).

Doubtless the transport numbers are not independent of the concentration of the acid, but it is not very probable that changes of the above magnitude are to be attributed to this circumstance alone.

It is well known that the Nernst formula giving the relation between *E.M.F.* and ionic concentration in such combinations is inaccurate, considerable divergencies between observed and calculated potentials being not unusual, and it seems probable that it is to this circumstance that the above apparent variations are mainly due. Any formula which may prove applicable must account for the striking fact that the value of E_3 is larger than E_6, although, a priori, the inverse was to be anticipated; as these two numbers are considerably larger than the others, and were consistently obtained within narrow limits, the authors attach most importance to them, and believe that further experiments are not likely to invert the general relationship.

When all considerations are carefully weighed, the most probable value for the transport number $1-n$ may still be considered to lie between 0·30 and 0·35 (compare Trans., 1911, **99**, 1420). It is hoped that direct measurements of the transport numbers now being undertaken in this laboratory will serve to place the values within relatively narrow limits.

Determination of the Temperature-coefficient of the Basic Water-value of Absolute Alcohol by means of the Hydrogen Electrode.

It has already been shown that influence of temperature on the basic water-value of absolute alcohol may be estimated either by measurements of the catalytic activity or by determination of the salt-forming power of hydrogen chloride in moist alcohol (Goldschmidt and Udby, *Zeitsch. Elektrochem.*, 1909, **15**, 7 and 8; Jones and Lapworth, Trans., 1911, **99**, 917 *et seq.*). Further, as the hydrogen electrode appears to furnish an independent method of estimating the approximate value of this constant, it appeared desirable to strengthen the practical foundation of the theory connecting the three apparently independent methods by measurements of the electromotive forces of the hydrogen electrode in moist alcohol at different temperatures.

The most satisfactory measurements previously recorded (Trans., 1911, **99**, 2250 and 2252) were made with 0·002*N*-hydrochloric acid in both compartments of the concentration cell, with 0·1*N*-lithium chloride a subsidiary electrolyte, and with varying small concentrations of water in one compartment only. The range of concentrations of water used in the experiments was somewhat narrow, and we have therefore repeated the measurements and extended them to include other concentrations of water. The apparatus used was similar to that employed in the earlier experiments, but the slide-wire bridge was replaced by the more accurate potentiometer already mentioned in the present paper (p. 2250). As before, constant potentials were rapidly attained, and readings were sharp and usually constant within 0·1 millivolt over periods of an hour or more. Results: at 25°:

Concentration cells with 0·002*N*-HCl and 0·100*N*-LiCl in both compartments; varying quantities of water in one compartment only.

The direction of the positive current was from the moist to the anhydrous solution inside the cell.

Potential (volts).	w = vol.-molecular concentration of water in moist solution.	P'/P = apparent ratio of hydrion concentrations.	r_{25} = basic water-value of absolute alcohol at 25°.
0·0226	0·222	0·415	*0·157*
0·0395	0·444	0·214	*0·121*
0·0482	0·666	0·153	*0·120*
0·0590	0·888	0·105	*0·104*
0·0625	1·000	0·0876	*0·096*

The potentials observed differ from those previously recorded by about 1 millivolt, except in the last line, where the discrepancy amounts to 3 millivolts. This represents, however, a not altogether unsatisfactory agreement, and is, except in the last instance, hardly much greater than might perhaps be accounted for by the errors made in the cruder volumetric measurements of the water added in the first series of experiments.

The following points are here worthy of note. First, the above numbers show clearly the same apparent fall in the value of r with increasing concentration of water, which has been shown to be characteristic of such cells made up without any subsidiary electrolyte; thus the view that the lithium chloride has an appreciable influence on the concentration of the "free" water is no longer so improbable as the remarks in the previous paper were intended to suggest, but investigations in this subject are now in progress, and with special reference to the value of r for catalysis in presence of lithium chloride.

Secondly, the maximum value is almost identical with the value of r deduced by Goldschmidt and Udby from experiments in catalysis in alcohol, whilst the last value is identical with that adopted as more probable by one of us in conjunction with his colleagues. The agreement is fortuitous, but it is interesting that the apparent range of results obtained in the various modes of estimating the value of this "constant" should so nearly coincide; it must be added that from the beginning of these experiments, normal concentration for the solutes has been the maximum limit.

In order to obtain values required for the temperature-coefficient of r by the hydrogen electrode method, measurements precisely similar to the above, but carried out at 0°, were undertaken, the apparatus being immersed in a large bath containing ice and water. Readings, especially at first, were less wholly satisfactory during this series, and it was found necessary frequently to repeat the numerous tedious operations involving purification of materials and apparatus before consecutive results, consistent even within 1 or

2 millivolts, were obtained. For this reason the whole series of observed potentials from thirty-nine different cells is given.

Results at 0°:

Conditions, other than temperature, were identical with those in the above series at 25°.

w.	Electromotive forces obtained, in millivolts.	Mean *E.M.F.* (volts).
0·222	(35·6, 26·1), 29·8, 29·9, 29·9, 30·2	0·0299
0·444	(49, 45·8), 48·1, 48·1, 49·7, 49·7, 49·7	0·0491
0·666	(52·9, 52·9, 56·8), 59·8, 61·7, (56·6), 60·5, 61·0, 61·0, 60	0·0606
0·888	(64·5, 64·4), 72, 72, 71·8, 72·5, 73·0, 71·8	0·0721
1·0	(65·4, 65·4, 76, 72), 76, 79·5, 79·5, 79·5	0·0786

The numbers which are bracketed on the table have been rejected in computing the mean values, but, with one exception, these neglected values represent those obtained at the beginning of the series of experiments.

From these numbers the apparent values of the relative concentration, P'/P, of "free" hydrogen ions in the moist as compared with that in the anhydrous solvent have been calculated, and thence the corresponding values of r_0, the apparent magnitude at 0° of the basic "water-value" of absolute alcohol containing lithium chloride of concentration $N/10$. The results are here tabulated for comparison with the corresponding values at 25°:

w = concentration of water.	*E.M.F.* in volts at 25°.	$r_{25°}$.	*E.M.F.* in volts at 0°.	$r_{0°}$.
0·222	0·0226	*0·157*	0·0299	*0·086*
0·444	0·0395	*0·121*	0·0491	*0·063*
0·666	0·0482	*0·120*	0·0606	*0·055*
0·880	0·0590	*0·104*	0·0721	*0·044*
1·000	0·0625	*0·096*	0·0786	*0·037*

Attention may be called to the following points in connexion with this table.

(1) Whilst with ordinary concentration cells the electromotive force increases nearly in proportion with the absolute temperature, cells of the above type decrease in electromotive force in agreement with the solvate theory as applied to moist alcoholic solutions of hydrogen chloride.

(2) The fall in the basic "water-value" of alcohol as estimated by means of the hydrogen electrode is of the same order as that deduced by chemical methods, but appears somewhat greater. Goldschmidt and Udby (*Zeitsch. Elektrochem., loc. cit.*) found by catalysis methods that r fell from 0·15 at 25° to 0·095 at 0°; in the above table (for $r=0·222$) the fall is 0·157 to 0·086. Jones and Lapworth (Trans., 1911, **99**, 937) deduced from the results obtained in two purely chemical methods the values 0·097 and 0·050 at 25° and 0° respectively as the most probable; in the above table (for $w=1·000$) the fall is from 0·096 to 0·036.

In the latter instance the discrepancy amounts to about 0·015 in the value of r, which corresponds with 0·015 gram-molecule of water per litre of alcohol. That is, the presence of 0·027 per cent. of water in one of the specimens of alcohol employed would be sufficient to account for the want of concordance in the figures given, so that, having regard only to the great difficulty always found in preparing and preserving alcohol in a quite anhydrous and otherwise approximately pure state, the result is almost as satisfactory as could reasonably be expected. It is clear again, however, that the presence of lithium chloride is not without appreciable influence, and from this point of view further study may lead to interesting results.

It may appropriately be mentioned here that whilst there appears to be no reason at present to modify the values of r at $N/50$-concentration of hydrogen chloride at 25° and at 0° already adopted, namely, 0·097 and 0·050 respectively, yet an extension of the measurements by tintometric methods already described suggest a value for r at 25° not exceeding 0·094, and at 0° one which lies between 0·04 and 0·045 for excessively dilute hydrogen chloride, and this would raise the value of q (the heat of hydrolysis of the alcoholated hydrogen ion) to about 5000 in gram-calories. The values of q, deduced from the experiments with the hydrogen electrode on the assumption that the values of r observed at 25° and at 0° with any given concentration of water may be introduced in the thermodynamic equation:

$$\log_e r - \log_e r' = \frac{q}{R}\left(\frac{1}{T'} - \frac{1}{T}\right),$$

vary between 3900 and 6100, increasing regularly with the amount of water present; the numbers so obtained are obviously of interest only inasmuch as they are of the same order of magnitude as the one derived from the more trustworthy modes of measurement.

The authors desire gratefully to acknowledge their indebtedness to the Grant Committees of the Royal and Chemical Societies for grants, from which much of the cost of this investigation was defrayed.

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CCXXXVI.—*Absorption Spectra of the Cobalto-derivatives of Primary Aliphatic Nitroamines.*

By Antoine Paul Nicolas Franchimont and
Hilmar Johannes Backer.

Several years ago one of us prepared the cobalto-derivatives of methylnitroamine and ethylnitroamine (Franchimont, *Rec. trav. chim.*, 1894, **13**, 324; 1897, **16**, 392). The curious properties of these salts led to the investigation of the same derivative of propylnitroamine. Cobaltomethylnitroamine, $Co(NMe{\cdot}NO_2)_2$, remains as a purple-violet, anhydrous, crystalline powder on evaporation of its aqueous solution at the ordinary temperature. Cobaltoethylnitroamine separates from its purple solution in beautiful yellowish-brown crystals containing two molecules of water. Cobaltopropylnitroamine forms large, bronze-green crystals, also with two molecules of water. Both these crystalline salts when powdered are only pale yellow in colour, and when dried over sulphuric acid or heated slightly, they pass into the purple anhydrous salts.

From cobaltomethylnitroamine no product containing water of crystallisation has been obtained. Dark-coloured, crystalline aggregates separate from a strongly-cooled concentrated solution, but when dried on filter paper they fall to a powder of the anhydrous salt. Possibly the hydrated form is only stable at a very low temperature.

Cobaltomethylnitroamine is readily soluble in water, the ethyl compound less so and the propyl compound still less so.

These three solutions, like the anhydrous salts—but in contradistinction to the compounds containing water of crystallisation—are coloured intensely purple-violet.

On heating, the solutions are hydrolysed with separation of blue, colloidal cobalt oxide.* To some extent the pure salts also undergo this hydrolysis on addition of water, so that the solutions always contain a slight excess of nitroamine.

In the ordinary organic solvents the cobaltonitroamines are almost insoluble.

When triturated in a mortar or heated, the anhydrous salts explode.

These observations remained isolated facts until the investigations of recent years on internal complex salts seemed to open up the possibility of gaining some insight into the constitution of these

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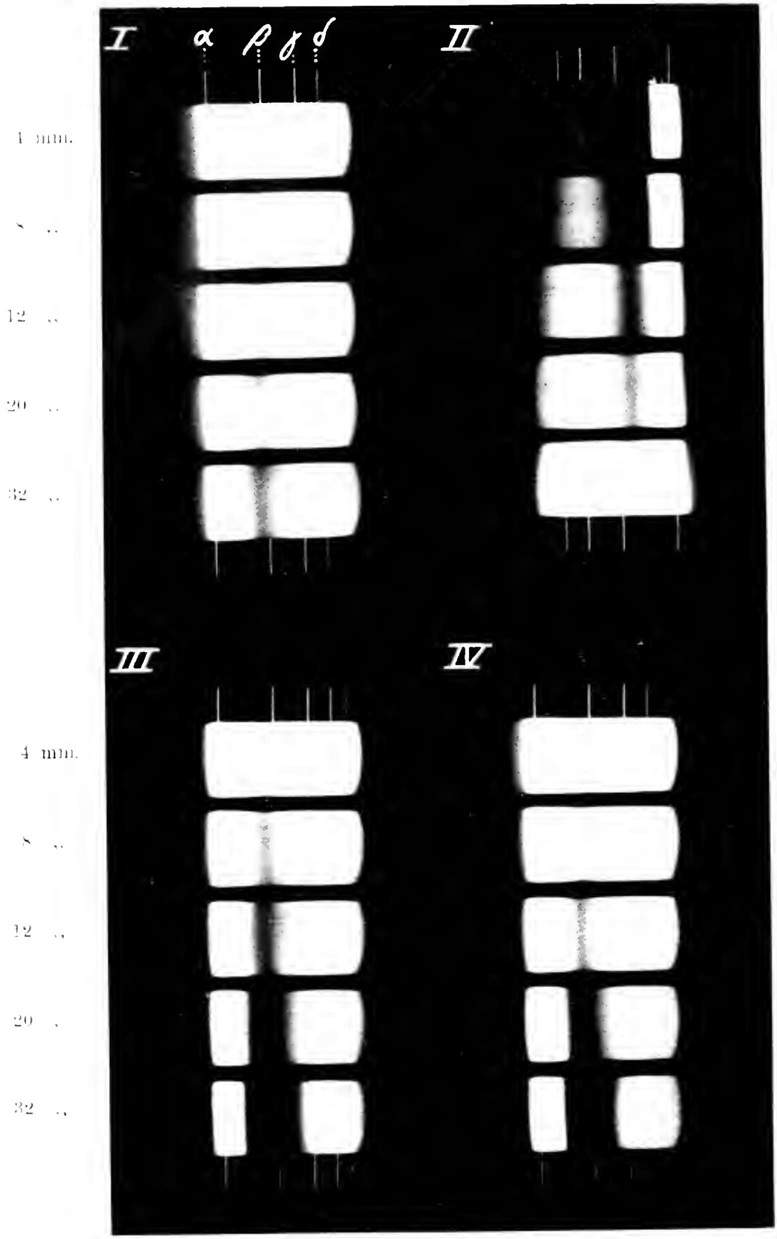
* It may be mentioned that the colourless zinc salts and the dark blue copper salts of the nitroamines are likewise decomposed when heated in aqueous solution.

22 b



Absorption spectra of aqueous solutions containing 0·1 *gram-atom* (=5·9 *grams*) *of cobalt per litre.*

I. *Cobalt nitrate.* II. *Cobaltomethylnitroamine.*
III. *Cobaltoethylnitroamine.* IV. *Cobaltopropylnitroamine.*

[*To face p.* 2257.

cobalt compounds, and also of adding to our knowledge of the nitroamines, as the structure of their metallic derivatives has not yet been sufficiently elucidated.*

With the view of obtaining objective and to some extent quantitative data concerning the light-absorbing power of these cobalt compounds, and—for comparison—also of a normal cobalt salt such as cobalt nitrate, the absorption spectra of their solutions were investigated photographically.

For this purpose Krüss's universal spectrum apparatus was used. The solutions contained all the same concentration of cobalt (0·1 gram-atom = 5·9 grams of cobalt per litre), and were investigated by means of a Baly-Desch tube in thicknesses of 4, 8, 12, 20, and 32 mm. Slit, exposure (three minutes †), temperature (20°), and source of light (incandescent electric lamp) were the same in all cases. The "Wratten" panchromatic plates were all developed in the same way, with an alkaline metol-hydroquinone solution. Above and under each plate the hydrogen spectrum was photographed for fixing the position of the absorption bands. The plate was measured by means of the spectra of hydrogen, mercury, sodium, thallium, and of the sun.

The measurement of the limits of absorption, which was carried out on the negatives, is always to some extent arbitrary, especially with bands terminating diffusely. An attempt was therefore made to treat all the spectra in the same way, so as to make the results comparable among themselves.

The absorption limits are given below in wave-lengths (millionths of millimetres), and, in view of the graphic representation, the reciprocals of the wave-lengths (in reciprocal millimetres) are also given.

I. *Cobalt Nitrate.*—Kahlbaum's nickel-free preparation was used. The absorption spectra are reproduced in Fig. 1. The narrow band does not become much wider with increasing thickness of the absorbing layer.

Thickness of layer, in mm.	Absorption limits.	
12	λ 513—498	$^1/\lambda$ 1949—2008
20	525—494	1905—2024
32	527—488	1898—2049

II. *Cobaltomethylnitroamine.*—This compound was prepared by shaking freshly precipitated and well washed cobaltous hydroxide with an aqueous solution of methylnitroamine. The anhydrous

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* The arguments for the different formulæ of the salts are given by Backer, "Die Nitramine und ihre Isomeren," Stuttgart, 1912, p. 73.

† The exposure should not be too short, as the plates show a minimum of sensibility near the absorption bands of the compounds studied.

salt remaining on evaporation at the ordinary temperature was washed with dry ether in order to remove any free nitroamine, then dissolved in water, filtered, and, after estimation of the cobalt, diluted to the desired concentration.

The spectrum (Fig. 2) shows an absorption which for small thicknesses occupies about the same place as with cobalt nitrate, but at greater thicknesses increases considerably in width. This absorption is sharply defined only on the side of long wave-lengths.

There further appears at greater thicknesses an absorption in the violet, proceeding to the other band.

Thickness of layer, in mm.	Absorption limits.	
8	λ 529—498	1/λ 1890—2008
12	559—485	1789—2062
20	572—465 and 409—	1748—2151 and 2445—
32	578—443 and 421—	1730—2257 and 2375—

III. *Cobaltoethylnitroamine.*—A crystallised product prepared by Mr. Folpmers from barium ethylnitroamine and cobalt sulphate. The aqueous solution was filtered, analysed, and diluted to the required concentration.

The absorption spectrum (Fig. 3) resembles that of cobaltomethylnitroamine, but there is no absorption in the violet.

Thickness of layer, in mm.	Absorption limits.	
8	λ 529—498	1/λ 1890—2008
12	549—491	1821—2037
20	564—470	1773—2128
32	574—452	1742—2212

IV. *Cobaltopropylnitroamine.*—A crystallised preparation made in the same way as the preceding substance. Some time was required to dissolve the necessary quantity (0·1 gram-molecule = 27·3 grams of crystallised salt) at room temperature.

The absorption spectrum shows great similarity to that of cobaltoethylnitroamine.

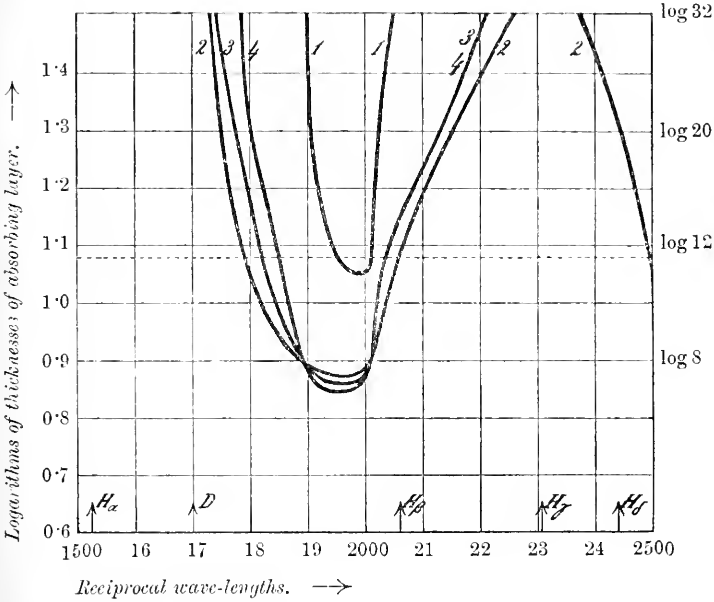
Thickness of layer, in mm.	Absorption limits.	
8	λ 529—498	1/λ 1890—2008
12	540—491	1852—2037
20	555—470	1802—2128
32	560—452	1786—2212

In Fig. 5 the measurements on the four cobalt compounds are represented graphically. The curves show for each of the compounds the relation between the logarithm of the absorbing thickness and the position of the absorption limits, expressed in reciprocal wave-lengths.

On inspecting the spectrum photographs (Figs. 1—4) or the graphic representation (Fig. 5) it is evident that the absorption by cobalt nitrate differs in character from that of the three nitroamine salts investigated. The principal absorption band is of the same type for all three compounds, although it increases somewhat with increasing molecular weight. In addition, cobaltomethylnitroamine shows a second absorption for shorter wave-lengths.

It is worthy of note that the difference between the first member and its homologues can be shown spectroscopically, and also reveals itself chemically by the different affinity for water.

Fig. 5.



Absorption curves of aqueous solutions containing 0·1 *gram-atom* (= 5·9 *grams*) *of cobalt per litre.*

1. *Cobalt nitrate.*
2. *Cobaltomethylnitroamine.*
3. *Cobaltoethylnitroamine.*
4. *Cobaltopropylnitroamine.*

The above observations seem to constitute an argument for the supposition that in the cobalt derivatives of the nitroamines the metal is attached to nitrogen, in contradistinction to the ordinary cobalt salts, such as cobalt nitrate. The different colour of the compounds containing water of crystallisation might possibly be attributed to formation of internal complex salts by means of the secondary valencies of the cobalt atom.

We hope soon to obtain further supports for this hypothesis, and then to give formulæ which will adequately account for the properties of the cobaltonitroamines.

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CCXXXVII.—*Pilosine: A New Alkaloid from* Pilocarpus microphyllus.

By FRANK LEE PYMAN.

PILOCARPINE, $C_{11}H_{16}O_2N_2$, its stereoisomeride *iso*pilocarpine, and pilocarpidine, $C_{10}H_{14}O_2N_2$, are the only alkaloids from the different varieties of jaborandi leaves which have been thoroughly characterised.

Pilocarpine and *iso*pilocarpine are found in most varieties. Pilocarpidine is obtained from *Pilocarpus jaborandi*, but according to Jowett (Trans., 1900, **77**, 473) does not occur in *P. microphyllus*.

Now, Herzig and Meyer (*Monatsh.*, 1898, **19**, 56) have shown that pilocarpidine does not contain an *N*-methyl group, and it is probable that this alkaloid is the parent base of pilocarpine containing an imino-group in the place of the *N*-methyl group. In accordance with this view it has been found that pilocarpidine, in common with other glyoxalines containing a free imino-group, gives a deep red coloration with sodium diazobenzene-*p*-sulphonate (Pauly's histidine reagent). It was then found that the mother liquors from *Pilocarpus microphyllus* containing the alkaloids remaining after the separation of pilocarpine and *iso*pilocarpine also gave a well-marked red coloration with sodium diazobenzene-*p*-sulphonate. A large quantity of such residues (representing many tons of leaves) being available it was thought of interest to subject them to a fresh investigation following the movements of the base containing the free imino-group with the help of this colour reaction.

After a lengthy and tedious process of separation, depending largely on the different solubilities of the bases in water, the residues gave (1) resinous matter, (2) a sparingly soluble oil giving an intense Pauly reaction, (3) a sparingly soluble crystalline base, which has been designated *pilosine*—this base, which was obtained in a yield amounting to 0·007 per cent. of the leaves, did not give the Pauly reaction; (4) a mixture of pilocarpine and *iso*pilocarpine; and (5) the mother liquor from (4), which contained the remaining readily soluble bases, and gave only a moderate Pauly reaction.

Pilocarpidine if present in these leaves would have been in fraction 5, but it was clear that the base responsible for the Pauly reaction was mainly concentrated into fraction 2, and it seemed not unlikely that the colour given by fraction 5 was due to the same compound. In any case, all attempts to isolate pilocarpidine from the last fraction were unsuccessful, and Jowett's statement that *P. microphyllus* does not contain pilocarpidine is thus confirmed.

The base contained in fraction 2, which gives the Pauly reaction, has not yet been isolated in a crystalline form, but the new crystalline alkaloid from the third fraction, *pilosine*, has been characterised and investigated.

Constitution of Pilosine and its Derivatives.

Pilosine has the empirical formula $C_{16}H_{18}O_3N_2$, and is a monacid optically active base. Its salts do not crystallise readily, but the following have been obtained in crystalline form: *sulphate*, $(C_{16}H_{18}O_3N_2)_2,H_2SO_4$; *hydrogen tartrate*, $C_{16}H_{18}O_3N_2,C_4H_6O_6$, and *aurichloride*, $C_{16}H_{18}O_3N_2,HAuCl_4$.

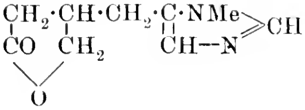
Pilosine gives no coloration with sodium diazobenzene-*p*-sulphonate; it contains an *N*-methyl, but no methoxyl group. It also contains a lactonic grouping, which accounts for two of the three oxygen atoms. The third oxygen atom occurs in the form of a hydroxyl group, for pilosine yields on treatment with acetic anhydride a new unsaturated base, *anhydropilosine*, $C_{16}H_{16}O_2N_2$, by the removal of the elements of water.

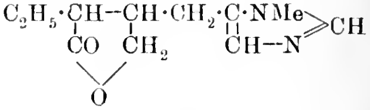
Anhydropilosine is a monacid, optically active base, forming beautifully crystalline salts, of which several have been prepared, and contains a lactonic grouping.

Pilosine dissolves in warm 5 per cent. aqueous potassium hydroxide, and can be recovered from this solution mainly unchanged, even after boiling for half an hour, although an odour of benzaldehyde indicating some decomposition is produced. When pilosine is distilled, however, with aqueous potassium hydroxide, kept at a strength of 20 per cent., for several hours, benzaldehyde passes over, and a new base, *pilosinine*, $C_9H_{12}O_2N_2$, remains in the alkaline liquid, the reaction being expressed by the following equation:

$$C_{16}H_{18}O_3N_2 = C_6H_5{\cdot}CHO + C_9H_{12}O_2N_2.$$

Pilosinine is a monacid, optically active, crystalline base, forming a well-crystallised *nitrate*, $C_9H_{12}O_2N_2,HNO_3$, and *hydrochloride*, $C_9H_{12}O_2N_2,HCl$. It contains an *N*-methyl group, and a lactonic grouping. It can be distilled unchanged, does not immediately decolorise aqueous acid permanganate, but decolorises bromine in chloroform solution. Its chemical properties are thus very similar to those of pilocarpine and *iso*pilocarpine; its solubilities, and physiological properties are also similar, and its parent compound, pilosine, occurs in the same plant which produces these glyoxaline derivatives. It is therefore highly probable that pilosinine itself is not only a glyoxaline derivative, but a lower homologue of pilocarpine and *iso*pilocarpine, having the constitutional formula given below:

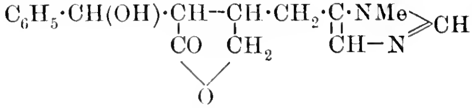

Pilosinine.


Pilocarpine.

Pilosinine is here represented as a 1:5-glyoxaline derivative owing to its connexion with pilocarpine and *iso*pilocarpine; there is, however, no direct evidence that it is a 1:5- rather than a 1:4-glyoxaline derivative.

The above formula satisfactorily accounts for all the known properties of pilosinine, and explains the similarity of its behaviour with that of pilocarpine and *iso*pilocarpine. It also permits of the construction of a probable formula for pilosine.

Since pilosine is decomposed into benzaldehyde and pilosinine on boiling with strong aqueous sodium hydroxide, and yields anhydropilosine when dehydrated by means of acetic anhydride, it must contain the grouping $C_6H_5\cdot CH(OH)$ attached to a carbon atom, which also bears a hydrogen atom. This grouping must, therefore, displace a hydrogen atom in one of the three methylene groups of the pilosinine molecule in such a way as to give rise to a formula for pilosine capable of explaining the ready decomposition of this alkaloid into pilosinine and benzaldehyde. This condition is fulfilled only in the case where pilosine is represented as derived from pilosinine by the displacement by $C_6H_5\cdot CH(OH)$ of one of the hydrogen atoms of the methylene group in the α-position with reference to the carboxylic group:


Pilosine.

for, if the $C_6H_5\cdot CH(OH)$ group substituted either of the other two methylene groups, it would give rise to compounds which would not be expected to decompose into benzaldehyde and pilosinine.

The formula for pilosine given above, however, represents pilosine as the lactone of a β-hydroxy-carboxylic acid, and it is well known that in certain circumstances β-hydroxy-acids are capable of decomposition in this manner.

Thus, β-hydroxy-acids, in which the α-carbon atom is doubly alkylated, yield on distillation an aldehyde and a carboxylic acid, for instance,

$$CH_3{\cdot}CH(OH){\cdot}CEt_2{\cdot}CO_2H = CH_3{\cdot}CHO + CHEt_2{\cdot}CO_2H$$

(compare Schnapp, *Annalen*, 1880, **201**, 70; Jones, *ibid.*, 1884, **226**, 287; and Blaise and Marcilly, *Bull. Soc. chim.*, 1904, [iii], **31**, 312).

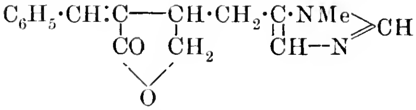
In the case of β-hydroxy-α-methyl(and ethyl)-butyric acids, however (compare Rohrbeck, *Annalen*, 1877, **188**, 229; and Waldschmidt, *ibid.*, 1877, **188**, 240), where the α-carbon atom is attached to a hydrogen atom—as in the case of pilosine—distillation leads to the formation of the corresponding unsaturated acid:

$$CH_3{\cdot}CH(OH){\cdot}CHMe{\cdot}CO_2H = CH_3{\cdot}CH{:}CMe{\cdot}CO_2H + H_2O.$$

It appears, nevertheless, that the mode of decomposition of β-hydroxy-acids, of which the α-carbon atoms are attached to a hydrogen atom, is influenced by the presence of a negative substituent such as the phenyl group; thus, Perkin (Trans., 1886, **49**, 160) has shown that an odour of benzaldehyde is developed on heating β-hydroxy-β-phenyl*iso*butyric acid. This indicates that the decomposition of this compound proceeds in some degree at least in accordance with the following equation:

$$C_6H_5{\cdot}CH(OH){\cdot}CHMe{\cdot}CO_2H = C_6H_5{\cdot}CHO + CH_2Me{\cdot}CO_2H.$$

The formula for pilosine given above is thus established with some degree of probability, and it is interesting to note that the $C_6H_5{\cdot}CH(OH)$ group in this alkaloid occupies the same position with regard to the rest of the molecule that the C_2H_5 group occupies in the case of pilocarpine and *iso*pilocarpine. This formula satisfactorily accounts for all the known properties of pilosine, and leads to the following formula for anhydropilosine:



$$C_6H_5{\cdot}CH{:}\underset{CO}{C}{-}\!\!{-}\underset{CH_2}{CH}{\cdot}CH_2{\cdot}\underset{CH{-}N}{C}{\cdot}NMe{>}CH \quad (CO{-}O{-}CH_2)$$

Anhydropilosine.

Specific Rotation of Pilosine and its Derivatives.

Pilocarpine, *iso*pilocarpine, and pilocarpidine are dextrorotatory in the form of base or salts with acids, and less dextrorotatory in the form of the alkali salts of the corresponding hydroxy-acid.

Pilosine and pilosinine are also dextrorotatory in the form of both base and salts with acids, whilst anhydropilosine is dextrorotatory as base, but lævorotatory as salt; all three alkaloids are lævorotatory in the form of the alkali salts of the corresponding hydroxy-acid.

The specific rotation of the three alkaloids as base, salt with acid, and salt with alkali calculated in each case for base is given below, together with the corresponding values for pilocarpine, *iso*pilocarpine, and pilocarpidine, calculated from Jowett's determinations.

Specific Rotation of Base as:

	Base.	Salt with acid.	Salt with alkali.
Pilocarpine	+100·5°	+108·0°	+31·5°
*iso*Pilocarpine	+42·8	+46·5	±0·0
Pilocarpidine	+81·3	+97·0	+35·2
Pilosine	+39·9	+24·6	−67·6
Anhydropilosine	+66·2	−20·8	−132·7
Pilosinine	+14·2	+5·8	−5·8

Jowett has shown that the difference between pilocarpine and *iso*pilocarpine is due to the change of sign of one of the two optically active carbon atoms, pilocarpine readily yielding *iso*pilocarpine on treatment with alkali. Now pilosine can be recovered mainly unchanged after boiling for some time with dilute aqueous sodium hydroxide, and it is therefore clear that pilosine and its derivatives correspond in stereochemical relations rather with *iso*pilocarpine than with pilocarpine.

Physiological Action of Pilosine and its Derivatives.

Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, kindly tested the physiological action of these alkaloids with the following results:

Pilosine has a very weak pilocarpine action, since it produces a typical but very weak inhibition of the cat's heart when given in 20 milligram doses. Anhydropilosine shows a similar behaviour.

Pilosinine has a mild pilocarpine action. It inhibits the heart of frogs and cats, and causes a fair reaction of saliva. It is somewhat stronger in this respect than pilosine, but it is still very much weaker than pilocarpine.

EXPERIMENTAL.

Isolation of Pilosine from Pilocarpus microphyllus.

The residual syrup from several tons of *Pilocarpus microphyllus* leaves from which the pilocarpine and *iso*pilocarpine had been removed as completely as possible during manufacture, was diluted with water, and fractionally precipitated with ammonia. This produced a precipitation, first of dark-coloured, then of light-coloured oil; the mother liquors, which gave no further turbidity on the addition of ammonia, were then extracted with chloroform, which removed a considerable amount of water-soluble alkaloid, from which pilocarpine and *iso*pilocarpine were isolated in the usual way, the mother liquor then returning to the fractionation process.

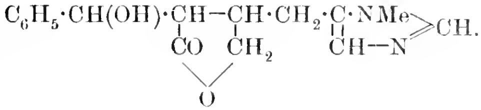
The dark- and light-coloured oils mentioned above were dissolved in dilute acid and again fractionally precipitated with ammonia, when the coloured impurities became largely concentrated in the earliest fractions. The later fractions of the sparingly soluble oil, when dissolved in a little alcohol, readily deposited crystals of a new alkaloid, *pilosine*, and the aqueous mother liquor gave up further quantities of water-soluble alkaloid to chloroform. The pilosine was purified by recrystallising from alcohol, and the mother liquors when they no longer deposited crystals were returned to the fractionation process, and the whole of these operations were again repeated many times.

Eventually, the following products were obtained: (1) non-basic or faintly basic, black, resinous matter; (2) a viscid syrup, sparingly soluble in water, giving an intense red coloration with Pauly's reagent; (3) a quantity of pilosine; these were obtained from the fractions precipitated as sparingly soluble oils on the addition of ammonia to the aqueous solutions of their salts.

From the chloroform extract of the mother liquors there were obtained: (4) a quantity of the mixed nitrates of pilocarpine and *iso*pilocarpine, and (5) a syrupy residue which gave a moderate red coloration with Pauly's reagent.

The results of the investigation, therefore, show that *Pilocarpus microphyllus*, which yields up to 0·99 per cent. of pilocarpine nitrate (Carr and Reynolds, *Pharm. J.*, 1908, **80**, 542) and small quantities of *iso*pilocarpine, contains also about 0·007 per cent. of pilosine. No other alkaloid is present in greater amount than 0·003 per cent. A sparingly soluble base giving the Pauly reaction is present, but this does not appear to be pilocarpidine.

Pilosine,



$$\begin{array}{l} C_6H_5\cdot CH(OH)\cdot CH-CH\cdot CH_2\cdot C\cdot NMe\!>\!CH. \\ \qquad\qquad\qquad\quad\; CO\quad CH_2 \qquad\; CH-N \\ \qquad\qquad\qquad\qquad\;\; O \end{array}$$

Pilosine crystallises from alcohol in large, colourless plates, which melt at 187° (corr.). It suffers no loss at 100°:

0·1516 gave 0·3722 CO_2 and 0·0864 H_2O. C = 66·9; H = 6·4.

0·1514 ,, 12·6 c.c. N_2 at 24° and 773 mm. N = 9·8.

$C_{16}H_{18}O_3N_2$ requires C = 67·1; H = 6·4; N = 9·8 per cent.

0·1272, titrated with dilute sulphuric acid using methyl-orange, required 4·4 c.c. $N/10$-H_2SO_4; whence equivalent = 289.

$C_{16}H_{18}O_3N_2$ requires M.W. = 286.

Pilosine is sparingly soluble in cold, fairly readily so in hot, water; sparingly soluble in cold, and easily so in hot, alcohol; and very sparingly soluble in boiling chloroform, ether, ethyl acetate, acetone, or benzene.

It dissolves readily in dilute acids, but not in cold dilute alkalis; it is soluble in hot aqueous sodium hydroxide. It gives no coloration with sodium diazobenzene-*p*-sulphonate.

Pilosine contains one NMe but no OMe group, since, on heating with hydriodic acid, methyl iodide is not eliminated below about 280°:

0·4436 gave 0·3598 AgI. NMe = 10·0.

$C_{15}H_{15}O_3N(NMe)$ requires NMe = 10·1 per cent.

The presence of a lactonic grouping was shown as follows:

A suspension of the base in cold water was rendered alkaline to phenolphthalein on the addition of a single drop of $N/10$-sodium hydroxide. After boiling, however, with excess of $N/10$-sodium hydroxide and titrating with $N/10$-sulphuric acid, it was found that 0·2328 required 8·1 c.c. $N/10$-NaOH, 8·1 c.c. being the required figure for one lactonic grouping, and the base was eventually recovered unchanged.

Pilosine, like pilocarpine and *iso*pilocarpine, is dextrorotatory, determinations of its specific rotation giving the following results:

in chloroform: α_D +0·94°; $l = 2$ dcm.; $c = 1·168$; $[\alpha]_D$ +40·2°;
in absolute alcohol: α_D +0·66°; $l = 2$ dcm.; $c = 0·827$; $[\alpha]_D$ +39·9°.

Pilocarpine is converted into its stereoisomeride *iso*pilocarpine by prolonged boiling with aqueous sodium hydroxide, and in order to determine whether pilosine underwent a similar change a quantity was boiled with excess of 5 per cent. aqueous sodium hydroxide for half an hour, then acidified with hydrochloric acid, and precipitated with ammonia. The base, which was obtained in nearly quantitative yield, was examined without further purification, when it melted at 187° (corr.), and gave the following result in chloroform solution:

α_D +0·61°; $l = 2$ dcm.; $c = 0·762$; $[\alpha]_D$ +40·0°.

Pilosine, therefore, is not readily altered by treatment with alkali, behaving in this respect like *iso*pilocarpine.

The specific rotatory power of pilocarpine falls from +100·5° to +31·5°, and that of *iso*pilocarpine from +42·8° to *nil* after remaining with excess of alkali, owing to the formation of salts of the corresponding hydroxy-acids; a similar change occurs even more markedly in the case of pilosine. After heating pilosine for ten minutes on the water-bath with two molecules of potassium hydroxide in aqueous solution, the following result was obtained:

α_D $-5·10°$; $l=2$ dcm.; $c=3·774$; $[\alpha]_D$ $-67·6°$.

The salts of pilosine do not crystallise readily on the whole, but the sulphate, acid tartrate, and aurichloride have been obtained in crystalline form. The hydrochloride, hydriodide, nitrate, picrate, and acid oxalate failed to crystallise on keeping.

Pilosine Sulphate.—On evaporating a neutral aqueous solution of pilosine sulphate to a viscid syrup, and stirring with absolute alcohol, this salt is obtained in crystalline form, and may be recrystallised from absolute alcohol. It separates in clusters of plates, which melt at 194—195° (corr.). This salt is very easily soluble in water, very sparingly so in cold absolute alcohol, and is anhydrous:

0·1486 gave 0·3128 CO_2 and 0·0780 H_2O. C=57·4; H=5·87.
0·1596 „ 0·0568 $BaSO_4$. $SO_4=14·6$.
$(C_{16}H_{18}O_3N_2)_2H_2SO_4$ requires C=57·3; H=5·7; $SO_4=14·3$ per cent.

A determination of the specific rotation in aqueous solution gave the following result:

α_D $+1·87°$; $l=2$ dcm.; $c=4·454$; $[\alpha]_D$ $+21·0°$.

Pilosine hydrogen tartrate remains as a syrup on evaporation of its aqueous solution; this becomes crystalline on stirring with absolute alcohol, and melts at 135—136° (corr.). It tends to separate from hot absolute alcohol at first as an oil, which gradually changes into prismatic crystals:

0·1792 gave 0·3606 CO_2 and 0·0912 H_2O. C=54·9; H=5·7.
$C_{16}H_{18}O_3N_2,C_4H_6O_6$ requires C=55·1; H=5·6 per cent.

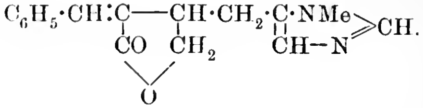
A determination of its specific rotatory power gave the following result:

α_D $+1·85°$; $l=2$ dcm.; $c=3·838$; $[\alpha]_D$ $+24·2°$.

Pilosine aurichloride was precipitated from an aqueous solution of the hydrochloride on the addition of gold chloride as an oil, which became partly crystalline on keeping. It crystallises from glacial acetic acid in clear, golden, wedge-shaped plates, which melt at 143—144° (corr.). This salt is very sparingly soluble in water or cold glacial acetic acid, and is anhydrous:

0·2047 gave 0·0641 Au. Au=31·3.
$C_{16}H_{18}O_3N_2,HAuCl_4$ requires Au=31·5 per cent.

Anhydropilosine,



Pilosine loses the elements of water when boiled for a short time with acetic anhydride; if undiluted acetic anhydride is used, a certain amount of charring takes place, and the quality and quantity of the resulting product, anhydropilosine, is unsatisfactory. On the other hand, boiling with glacial acetic acid does not dehydrate pilosine. By boiling pilosine, however, for a short time with a mixture of equal volumes of acetic anhydride and glacial acetic acid, anhydropilosine is readily obtained in nearly theoretical yield.

Ten grams of pilosine, 20 c.c. of glacial acetic acid, and 20 c.c. of acetic anhydride were boiled for half-an-hour under a reflux condenser. The product was diluted with water, and mixed with a slight excess of ammonia, when most of the anhydropilosine was precipitated, and became crystalline on seeding and stirring; the remainder was obtained by extracting the liquor with chloroform. Anhydropilosine crystallises from ethyl acetate in clusters of colourless rods, which melt at 133—134° (corr.). It suffers no loss at 100°:

0·1682 gave 0·4400 CO_2 and 0·0896 H_2O. C=71·4; H=6·0.

$C_{16}H_{16}O_2N_2$ requires C=71·6; H=6·0 per cent.

Anhydropilosine is sparingly soluble in cold, readily so in hot, water; it is very readily soluble in alcohol, acetone, benzene, chloroform, or warm ethyl acetate; fairly readily so in cold ethyl acetate, and sparingly soluble in ether. Unlike pilosine, it immediately decolorises aqueous permanganate.

The presence of a lactonic grouping in this compound was shown, as in the case of pilosine:

0·1805 required 6·4 c.c. $N/10$-NaOH, 6·7 c.c. being required for one lactonic grouping.

Anhydropilosine is dextrorotatory, a determination of its specific rotation in 95 per cent. alcohol giving the following result:

α_D +4·73°; l=2 dcm.; c=3·571; $[\alpha]_D$ +66·2°.

After heating anhydropilosine for ten minutes in the water-bath with two molecules of potassium hydroxide in aqueous solution, the following result was obtained:

α_D −8·34°; l=2 dcm.; c=3·142; $[\alpha]_D$ −132·7°.

Anhydropilosine forms salts which crystallise readily.

Anhydropilosine sulphate separates from absolute alcohol in clusters of prisms, which melt at 174° (corr.) after sintering a few degrees earlier. It is anhydrous, and is very easily soluble in water, but sparingly so in cold absolute alcohol:

0·1658 gave 0·3652 CO_2 and 0·0823 H_2O. C=60·1; H=5·5.
$(C_{16}H_{16}O_2N_2)_2,H_2SO_4$ requires C=60·5; H=5·4 per cent.

A determination of its specific rotatory power in aqueous solution gave the following result:

α_D −1·43°; l=2 dcm.; c=4·064; $[\alpha]_D$ −17·6°.

Anhydropilosine nitrate crystallises from water in large, tabular prisms, which melt and decompose at 153—154° (corr.). It is anhydrous, and is very readily soluble in water, but sparingly so in cold alcohol:

0·1605 gave 0·3405 CO_2 and 0·0734 H_2O. C=57·8; H=5·1.
$C_{16}H_{16}O_2N_2,HNO_3$ requires C=58·0; H=5·2 per cent.

A determination of its specific rotatory power in aqueous solution gave the following result:

α_D −1·38°; l=2 dcm.; c=3·806; $[\alpha]_D$ −18·1°.

Anhydropilosine hydrogen oxalate crystallises from alcohol in clusters of flat needles, which melt at 153—154° (corr.). It is anhydrous, and is very easily soluble in water, but sparingly so in cold alcohol:

0·1726 gave 0·3802 CO_2 and 0·0800 H_2O. C=60·1; H=5·2.
$C_{16}H_{16}O_2N_2,C_2H_2O_4$ requires C=60·3; H=5·1 per cent.

A determination of its specific rotatory power in aqueous solution gave the following result:

α_D −1·46°; l=2 dcm.; c=4·093; $[\alpha]_D$ −17·8°.

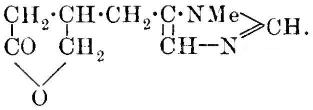
Action of 20 per Cent. Potassium Hydroxide on Pilosine. Formation of Pilosinine and Benzaldehyde.

Twenty grams of pilosine were distilled with a solution of 50 grams of potassium hydroxide in 250 c.c. of water, the level of the liquid in the distillation flask being kept constant by the addition of water from a tap-funnel. The condensed distillate contained drops of benzaldehyde during the first few minutes only, but after eleven hours' continuous distillation, when some 4 litres had been collected, the distillate still had the characteristic odour of benzaldehyde, and gave a faint turbidity with aqueous phenylhydrazine acetate.

The distillation was stopped at this point, and the whole of this distillate mixed with an excess of aqueous phenylhydrazine acetate, when 9·6 grams of benzaldehydephenylhydrazone (m. p. 158°. Found, C=79·5; H=6·2. Calc., C=79·5; H=6·2 per cent.) were obtained, that is, 70 per cent. of the theoretical yield.

The colourless alkaline distillation residue was acidified by the addition of 100 grams of 50 per cent. sulphuric acid, boiled for five minutes (to cause lactone formation), then made alkaline with ammonia, and filtered from a little insoluble matter. The ammoniacal solution was then completely extracted with chloroform, and the latter distilled, when a quantity of nearly pure pilosinine base was obtained. This was crystallised as nitrate, and gave 10·0 grams of the pure salt. The ammoniacal liquor still contained a further quantity of pilosinine as the ammonium salt of the corresponding hydroxy-acid, and was therefore again boiled with dilute mineral acid, made alkaline with ammonia, and extracted with chloroform, this process being again repeated. The additional quantities of pilosinine thus obtained gave another 2·8 grams of the pure nitrate, so that 12·8 grams of this salt were obtained in all, that is, 75 per cent. of the theoretical yield. The ultimate mother liquors when again distilled with concentrated aqueous potassium hydroxide and worked up as before, gave a further quantity of pilosinine nitrate.

Pilosinine,



$$\begin{array}{l} CH_2\cdot CH\cdot CH_2\cdot C\cdot NMe \\ \; | \qquad\;\; | \qquad\qquad\; \| \qquad\qquad > CH. \\ CO \quad CH_2 \qquad\; CH{-}N \\ \quad \diagdown\!\diagup \\ \quad\; O \end{array}$$

This base is isolated by extraction with chloroform from a solution of the nitrate made alkaline with ammonia. After removal of the solvent it remains as an oil, which becomes crystalline on stirring. It crystallises from anhydrous ethyl acetate in broad needles or plates, which melt at 78—79° (corr.):

0·1640 * gave 0·3585 CO_2 and 0·0974 H_2O. C = 59·6; H = 6·6.

$C_9H_{12}O_2N_2$ requires C = 60·0; H = 6·7 per cent.

Pilosinine is slightly deliquescent, very readily soluble in water, alcohol, chloroform, or acetone; moderately soluble in cold, and readily in hot, ethyl acetate, and sparingly soluble in dry ether. It distils in the neighbourhood of 300°/35 mm., passing over as a nearly colourless oil, which crystallises on seeding. It does not immediately decolorise aqueous acid permanganate, and gives no coloration with sodium diazobenzene-*p*-sulphonate. It decolorises bromine in chloroform solution, an insoluble, brown oil (perbromide) separating from the solution, as in the case of other glyoxaline derivatives.

The presence of a lactonic grouping in this compound was shown, as in the case of pilosine:

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* Dried in a vacuum.

0·1821 required 10·1 c.c. $N/10$-NaOH, 9·7 c.c. being required for one lactonic grouping.

Pilosinine is dextrorotatory, a determination of its specific rotatory power in a freshly-made-up aqueous solution giving the following result:

$$\alpha_D +1{\cdot}15^\circ;\ l=2 \text{ dcm.};\ c=4{\cdot}062;\ [\alpha]_D +14{\cdot}2^\circ.$$

The rotation of aqueous solutions of pilosinine, however, rapidly sinks on keeping, doubtless owing to the gradual conversion of the lactone into the corresponding hydroxy-acid; thus the specific rotatory power of the solution mentioned above was redetermined, after keeping, with the following results:

after twenty-four hours, $[\alpha]_D +9{\cdot}8^\circ$,
after forty-eight hours, $[\alpha]_D +7{\cdot}8^\circ$,
after five days, ... $[\alpha]_D +3{\cdot}1^\circ$.

This behaviour is analogous to that of pilocarpine, of which the rotation in 7 per cent. aqueous solution fell from $+100{\cdot}5^\circ$ to $+77{\cdot}5^\circ$ after keeping for three weeks according to Jowett (Trans., 1900, **77**, 481).

After heating pilosinine for ten minutes in the water-bath with two molecules of aqueous potassium hydroxide, the following result was obtained:

$$\alpha_D -0{\cdot}44^\circ;\ l=2 \text{ dcm.};\ c=3{\cdot}941;\ [\alpha]_D -5{\cdot}8^\circ.$$

Pilosinine nitrate crystallises from water in large, clear, colourless prisms, which melt at 165—167° (corr.). It is soluble in about 2·5 parts of cold water, readily soluble in hot water, but sparingly so in alcohol. It is anhydrous:

0·1668 gave 0·2700 CO_2 and 0·0821 H_2O. C = 44·2; H = 5·5.
0·1406 ,, 21·2 c.c. N_2 at 24° and 766 mm. N = 17·6.
$C_9H_{12}O_2N_2,HNO_3$ requires C = 44·4; H = 5·4; N = 17·3 per cent.

A determination of its specific rotation in aqueous solution gave the following result:

$$\alpha_D +0{\cdot}73^\circ;\ l=2 \text{ dcm.};\ c=8{\cdot}412;\ [\alpha]_D +4{\cdot}3^\circ.$$

Pilosinine hydrochloride separates from water and alcohol in prismatic crystals, which melt at 218—219° (corr.). It is readily soluble in water, but somewhat sparingly so in cold alcohol:

0·2670 gave 0·1765 AgCl. Cl = 16·4.
$C_9H_{12}O_2N_2,HCl$ requires Cl = 16·4 per cent.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

CCXXXVIII.—*The Effect of Heat on a Mixture of Benzaldehydecyanohydrin with* m-*Chloroaniline and with* m-*Toluidine.*

By CLEMENT WILLIAM BAILEY (Priestley Research Scholar of the University of Birmingham) and HAMILTON McCOMBIE.

EVEREST and McCombie (Trans., 1911, **99**, 1752) have described the effect of heat on a mixture of aniline and benzaldehydecyanohydrin, and have shown that the following compounds are the main products of the reaction: (1) Anilinophenylacetonitrile, NHPh·CHPh·CN; (2) dibenzoyldianilinostilbene,

NPhBz·CPh⁚CPh·NPhBz;

and (3) 1:3:5-triphenylglyoxaline, $C_{27}H_{20}N_2$.

The constitution of (2) was established by a series of decompositions, first with sodium hydroxide, when monobenzoyldianilinostilbene resulted, and this compound was then found to decompose in chloroform solution to yield benzanilide and dibenzanilide in molecular proportions.

In order to extend the reaction to the case of substituted anilines, to see whether the reaction was a general one for primary aromatic amines, the reaction was investigated when the three chloroanilines were substituted for aniline.

When *o*-chloroaniline and benzaldehydecyanohydrin were heated together under conditions similar to those employed by Everest and McCombie, no crystalline products could be isolated from the reaction mixture. This is probably due to the fact that under these conditions the *o*-chloro-analogue of anilinophenylacetonitrile is not formed. Further, it was found impossible to cause *o*-chloroaniline to condense with benzoin to form α-keto-β-*o*-chloroanilino-αβ-diphenylethane, $COPh \cdot CHPh \cdot NH \cdot C_6H_4Cl$. The formation of both of these compounds seems to be essential to the formation of the higher stilbene molecule.

In the case of *m*-chloroaniline, the reaction was found to proceed in a manner exactly analogous to that in which aniline was used. The products were: (1) *m*-Chloroanilinophenylacetonitrile, $C_6H_4Cl \cdot NH \cdot CHPh \cdot CN$; (2) dibenzoyldi-*m*-chloroanilinostilbene, $C_6H_4Cl \cdot NBz \cdot CPh{:}CPh \cdot NBz \cdot C_6H_4Cl$; (3) 1:5-diphenyl-3-*m*-chlorophenylglyoxaline, $C_{27}H_{19}N_2Cl$; and (4) α-keto-β-*m*-chloroanilino-αβ-diphenylethane, $C_{20}H_{16}ONCl$.

Compound (2) on decomposition by potassium hydroxide yielded benzoic acid and monobenzoyldi-*m*-chloroanilinostilbene,

$$C_6H_4Cl \cdot NH \cdot CPh{:}CPh \cdot NBz \cdot C_6H_4Cl.$$

This compound in chloroform solution underwent atmospheric oxidation, yielding benzo-*m*-chloroanilide and dibenzo-*m*-chloroanilide, in accordance with the following equation:

$$C_{33}H_{25}ON_2Cl + O_2 = NBz_2 \cdot C_6H_4Cl + NHBz \cdot C_6H_4Cl.$$

When *p*-chloroaniline was employed, the reaction took a different form, and the product obtained, when crystallised from pyridine, gave analytical figures which are in agreement with the empirical formula $C_{35}H_{24}O_3N_2Cl_2$.

Further investigations were carried out with a view to determining whether the anomalous behaviour displayed by the chloroanilines was peculiar to them. For this purpose the three toluidines were used, with the following results: From *o*-toluidine no products could be obtained; from *m*-toluidine the products were analogous to those obtained when *m*-chloroaniline and aniline were employed; from *p*-toluidine the product was analogous to that obtained from *p*-chloroaniline, and the analytical figures correspond with the formula $C_{37}H_{30}O_3N_2$, which will be seen to be analogous to that of the compound obtained from *p*-chloroaniline, if a methyl group is substituted for each chlorine atom.

Thus it will be seen that the reaction described by Everest and McCombie is not a general one for primary aromatic amines, since meta- and para-substituted anilines seem to behave in different ways. The meta-isomerides in the two cases investigated behave like the unsubstituted aniline, whilst in the case of the para-compounds the reaction seems to take a different form.

As the work has to be interrupted at this stage, the constitution of the products obtained from the para-compounds cannot be determined at the present moment, but we hope to publish the completed work at a future date.

EXPERIMENTAL.

m-*Chloroanilinophenylacetonitrile*, $C_{14}H_{11}N_2Cl$.

Equimolecular proportions of *m*-chloroaniline and benzaldehydecyanohydrin were heated together for two hours to 130°. Water was eliminated, and the mass solidified on cooling. It is soluble in all ordinary organic solvents, and crystallises from alcohol in colourless, diamond-shaped plates, melting at 68°:

0·3526 gave 0·2070 AgCl. Cl=14·56.

$C_{14}H_{11}N_2Cl$ requires Cl=14·62 per cent.

s-*Dibenzoyldi*-m-*chloroanilinostilbene*, $C_{40}H_{28}O_2N_2Cl_2$.

Equimolecular quantities of *m*-chloroaniline and benzaldehydecyanohydrin were heated for two hours to 130°. To the mixture was then added a slight excess of benzaldehyde, and the heating was continued until a large aggregate of cubical crystals separated out in the boiling liquid. This usually required twenty-four to sixty hours. The solid was collected and extracted with ether in a Soxhlet extractor. It is a hard, brittle, colourless substance, and melts and decomposes at 350°.

It is soluble in alcohol or acetic acid, but insoluble in ether or acetone. It was found impossible to crystallise this substance from any solvent, and therefore it has not been obtained in a very pure state:

0·160 gave 0·433 CO_2 and 0·0666 H_2O. C=73·7; H=4·6.
0·247 „ 8·9 c.c. N_2 at 15° and 731 mm. N=4·03.
0·202 „ 0·0938 AgCl. Cl=11·5.
$C_{40}H_{28}O_2N_2Cl_2$ requires C=75; H=4·3; N=4·3; Cl=11·1 per cent.

This substance was also prepared by heating together equimolecular quantities of α-keto-β-benzoyl-*m*-chloroanilino-αβ-diphenylethane and *m*-chloroaniline with a small quantity of potassium cyanide for twenty-four to sixty-nine hours to 150°. The mass was extracted with benzene, in which the required product was insoluble. The remaining product was benzo-*m*-chloroanilide.

Monobenzoyldi-m-*chloroanilinostilbene*, $C_{33}H_{24}ON_2Cl_2$.

This compound was prepared by adding a small quantity of potassium hydroxide to an alcoholic solution of the dibenzoyl compound. The mixture was then heated for one hour, and the monobenzoyl compound which separated out as a yellow precipitate was collected and washed with hot water.

It could not be crystallised, as it was unstable when in solution. It melts at 200°, and is soluble in chloroform, acetone, acetic acid, or amyl alcohol; insoluble in ether; and sparingly soluble in alcohol:

0·2176 gave 0·5910 CO_2 and 0·0899 H_2O. C=74·01; H=4·59.
0·1985 „ 0·1035 AgCl. Cl=12·9.
$C_{33}H_{24}ON_2Cl_2$ requires C=74·0; H=4·5; Cl=13·2 per cent.

Quantitative Decomposition of Dibenzoyldi-m-*chloroanilinostilbene.*

Three to 4 grams were heated under reflux with 25 c.c. of *N*-potassium hydroxide in the presence of alcohol. The excess of alkali was estimated in the filtrate:

5 grams gave 0·85 benzoic acid. Required 0·92 benzoic acid.

Monobenzoyldi-m-*chloroanilinostilbene Hydrochloride.*—This was prepared by passing a stream of dry hydrogen chloride through an acetic acid solution of the base. It separates in small cubes, and is recrystallised from acetic acid. It does not melt, and the base is regenerated by alkali:

0·1888 gave 0·1440 AgCl. Cl = 18·8.

$C_{33}H_{24}ON_2Cl_2,HCl$ requires Cl = 18·65 per cent.

The *platinichloride* was prepared by adding a solution of platinum tetrachloride to a solution of the above-described hydrochloride in acetic acid. It is slightly pink in colour:

0·100 gave 0·0079 Pt. Pt = 12·7.

$(C_{33}H_{24}ON_2Cl_2,HCl)_2,PtCl_4$ requires Pt = 13·1 per cent.

*Compound of Monobenzoyldi-*m*-chloroanilinostilbene with Picric Acid.*

This was obtained by adding a solution of picric acid in acetic acid to one of the base in the same solvent.

It crystallised out in a short time, and was recrystallised from acetic acid. It is deep yellow, and appears as small needles, which melt at 246°:

0·2580 gave 0·5910 CO_2 and 0·079 H_2O. C = 62·5; H = 3·40.
0·1920 ,, 15·9 c.c. N_2 at 14° and 762 mm. N = 9·69.
$(C_{33}H_{24}ON_2Cl_2 + C_6H_3O_7N_3) - H_2O$ requires C = 62·7; H = 3·40; N = 9·53 per cent.

*Decomposition of Monobenzoyldi-*m*-chloroanilinostilbene in Solution.*

A quantity of the base was dissolved in each of the three solvents acetone, chloroform, and amyl alcohol, and the solutions were allowed to remain in flasks with access to the air. The solutions darkened slowly, and crystals of dibenzo-*m*-chloroanilide appeared. On collecting these and concentrating the solutions, a quantity of benzo-*m*-chloroanilide was obtained. No other product was obtained except in the case of the amyl-alcoholic solution, when a quantity of dibenzoyldi-*m*-chloroanilinostilbene was found.

Decomposition of the Base by Heat.

A quantity of the base was heated to 150° for two hours, when it assumed a pasty consistency. On extracting with benzene the residue was found to be dibenzoyldi-*m*-chloroanilinostilbene, whilst the soluble portion was benzo-*m*-chloroanilide.

*Dibenzo-*m*-chloroanilide,* $C_{20}H_{14}O_2NCl$.

This was prepared for the purpose of identifying the product obtained from the decomposition of the base. It was obtained by heating equimolecular proportions of benzo-*m*-chloroanilide and benzoyl chloride for four hours to 200°.

It was crystallised from alcohol, from which it separates in almost colourless cubes melting at 132°:

0·1876 gave 0·4895 CO_2 and 0·0720 H_2O. C=71·0; H=4·27.
$C_{20}H_{14}O_2NCl$ requires C=71·4; H=4·17 per cent.

*α-Keto-β-*m*-chloroanilino-αβ-diphenylethane,* $C_{20}H_{16}ONCl$.

This compound was prepared by heating together for eight hours equimolecular proportions of benzoin and *m*-chloroaniline in a sealed tube to 200°. The product was crystallised from alcohol, from which it separated in faintly yellow prisms melting at 130°.

The compound appears as a by-product in the preparation of dibenzoyldi-*m*-chloroanilinostilbene:

0·2196 gave 0·6022 CO_2 and 0·1079 H_2O. C=74·8; H=5·46.
0·1935 ,, 0·084 AgCl. Cl=10·8.
$C_{20}H_{16}ONCl$ requires C=74·8; H=5·0; Cl=10·9 per cent.

*α-Keto-β-benzoyl-*m*-chloroanilino-αβ-diphenylethane,* $C_{27}H_{20}O_2NCl$.

This was prepared from the above by the ordinary Schotten-Baumann reaction. It was crystallised from alcohol, when it separated in colourless prisms melting at 122°:

0·1899 gave 0·5291 CO_2 and 0·0829 H_2O. C=76·0; H=4·85.
0·2264 ,, 0·0751 AgCl. Cl=8·2.
$C_{27}H_{20}O_2NCl$ requires C=76·1; H=4·7; Cl=8·3 per cent.

2:4:5-*Triphenyl*-1-m-*chlorophenylglyoxaline,* $C_{27}H_{19}N_2Cl$.

This compound was prepared by heating together 5 grams of α-keto-β-benzoyl-*m*-chloroanilino-αβ-diphenylethane with 5 c.c. of aqueous ammonia (D 0·880) in a sealed tube for eight hours to 230°. The product was extracted with ether to remove tars.

The glyoxaline crystallised from alcohol in fine, fluffy needles, melting at 210°.

This compound also appears as a by-product in the preparation of dibenzoyldi-*m*-chloroanilinostilbene; it separates out from the tarry residues after about one week:

0·8568 gave 0·4536 CO_2 and 0·0706 H_2O. C=78·9; H=5·0.
0·1385 ,, 0·0478 AgCl. Cl=8·55.
$C_{27}H_{19}N_2Cl$ requires C=79·7; H=4·68; Cl=8·7 per cent.

s-*Dibenzoyldi*-m-*toluidinostilbene*, $C_{42}H_{34}O_2N_2$.

This compound was prepared by a method exactly similar to that used for the preparation of the *m*-chloro-compound. Equimolecular proportions of *m*-toluidine and benzaldehydecyanohydrin were heated together for twelve hours, and then excess of benzaldehyde was added, and the heating continued for a further period of twenty-four hours, when crystals of the required product began to appear in the boiling liquid. The deposition of solid ceased after about twelve hours, thus making a total heating of from forty-eight to sixty hours.

The compound was collected, and washed with ether in a Soxhlet extractor for twelve hours. It was then in the form of a white, brittle powder, and was used in this form for the purposes of analysis as it was found impossible to crystallise it from any solvent. It melted at about 360°:

0·2336 gave 0·7198 CO_2 and 0·1198 H_2O. C=84·0; H=5·70.

$C_{42}H_{34}O_2N_2$ requires C=84·3; H=5·69 per cent.

Monobenzoyldi-m-*toluidinostilbene*, $C_{35}H_{30}ON_2$.

This compound was prepared by adding a small quantity of aqueous potassium hydroxide to an alcoholic solution of the dibenzoyl compound described above.

It differs from the *m*-chloro-derivative in that it melts at a much lower temperature, and that it is soluble in alcohol, and can be recrystallised from this solvent without decomposition. It decomposes in solution in other solvents in exactly the same manner as does the *m*-chloro-analogue.

It crystallises from ethyl alcohol as a very fine, yellow powder, melting at 159°:

0·1792 gave 0·5575 CO_2 and 0·1002 H_2O. C=84·8; H=6·2.

$C_{35}H_{30}ON_2$ requires C=85·0; H=6·07 per cent.

Monobenzoyldi-m-*toluidinostilbene Hydrochloride.*

This compound can be prepared by saturating an acetic acid solution of the monobenzoyl compound with dry hydrogen chloride, but it was more readily obtained from an alcoholic solution of the dibenzoyl compound on account of the solubility of the hydrochloride in acetic acid.

It was crystallised from alcohol, from which it separates in small, white, cubical crystals:

0·2736 gave 0·0750 AgCl. Cl=6·78.

$C_{35}H_{30}ON_2,HCl$ requires Cl=6·70 per cent.

*Compound of Monobenzoyldi-*m*-toluidinostilbene with Picric Acid.*

This compound was also more readily obtained from the dibenzoyl than from the monobenzoyl compound, on account of the extreme solubility of the product in acetic acid.

Alcoholic solutions of the dibenzoyl compound and of picric acid were united, and the mixture boiled for a short time.

The compound crystallised out on cooling in deep yellow prisms, which on recrystallisation from alcohol melted at 218°:

0·1936 gave 0·4948 CO_2 and 0·0780 H_2O. C=69·7; H=4·48.
$(C_{35}H_{30}ON_2+C_6H_3O_7N_3)-H_2O$ requires C=69·8; H=4·40 per cent.

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CCXXXIX.—*The Ignition of Electrolytic Gas by the Electric Discharge.*

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THE ignition of a gas mixture is usually brought about by raising some portion of it to a sufficiently high temperature. The lowest temperature at which the rapid inflammation of a gas mixture occurs, in the absence of a catalyst, is the ignition-temperature of that mixture. It is well known, however, that small portions of an inflammable gas mixture may be heated many hundred degrees above its ignition-temperature without ignition taking place (compare Mallard and Le Chatelier, *Ann. des Mines*, 1883, [viii], **4**, 289). A simple experiment illustrates this. If a thread of cordite is ignited it gradually burns with a ball of flame of about 1 cm. diameter. This flame may be blown out, but nevertheless the cordite continues to consume away, emitting a spray of sparks which do not re-ignite the gaseous envelope, and cannot ignite a coal gas jet, in spite of their obviously high temperature. The success of the cerium-iron alloy, which on rubbing along a file throws off burning particles capable of igniting coal gas, depends probably on the great size of these sparks. They are large enough to heat a bulk of gas sufficiently great to initiate a flame.

In spite of the interest attaching to the phenomenon of ignition, our knowledge of the subject has not increased much since the investigations of Sir Humphry Davy were published (*Phil. Trans.*, 1816, 1, 115; 1817, 45, 77). Ignition-temperatures, it is true, have been determined in numerous ways, and that subject may be regarded as fairly well understood. The limits of inflammability of many gas mixtures at atmospheric pressure have been determined by various experimenters, but although these limits are regarded in each case as being sharply defined, yet when the results of different workers are compared they are seen to differ widely; for example, the lower limit of inflammability of hydrogen-air mixtures has been given from as low as 4·5 per cent. to as much as 10·0 per cent. hydrogen; and the upper limit from 55 per cent. to 80 per cent. hydrogen.

In order to obtain some information on the circumstances governing the initiation of a flame, the experiments quoted below were begun. A measure of the inflammability of combustible gas mixtures was sought in a determination of the minimum pressure necessary for the production of a flame. The first "ignition-pressure" to be measured was that for electrolytic gas ($2H_2+O_2$), a number determined previously by Meyer and Seubert (Trans., 1884, **45**, 581) as 125 mm. for a certain spark, 72 mm. for a stronger spark *; by Dixon (*Phil. Trans.*, 1884, **175**, 634) as between 70 and 75 mm. for a particular spark passing through electrolytic gas mixed with its own volume of air; by De Hemptinne (*Bull. Acad. Roy. Belg.*, 1902, 761) as varying erratically between 34 and 85 mm.; by Fischer and Wolf (*Ber.*, 1911, **44**, 2956) as 146 mm., the mean of several determinations.

The experiments quoted below soon showed that the ignition-pressure of electrolytic gas depends very greatly on the nature of the discharge as determined by the amount of electricity and by the condition of the electrodes. Hence the ignition-pressure is a measure of the igniting power of a definite spark; it is the minimum pressure required for the initiation of a flame in the region of the particular spark employed, not necessarily the minimum for the propagation of a flame already started.

EXPERIMENTAL.

A number of glass vessels of chosen sizes and shapes were each provided with four platinum electrodes fused in position to give sparks of 1 mm. and 5 mm. length, and also sparks running through the whole length of the vessel. Each vessel was sealed to a tap connecting by fused glass joints to a mercury pressure gauge, a

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* This term has been commonly employed in scientific papers to describe a luminous electric discharge in a gas; at pressures of the order quoted, the discharge is of the nature of a brush or glow.

mercury Sprengel pump for exhaustion, and through long U-tubes packed with solid potassium hydroxide to a gas-holder containing electrolytic gas. The gas was obtained by electrolysis of a hot solution of recrystallised barium hydroxide. A Ruhmkorff coil capable of giving a two-inch spark in air was used for the earlier experiments.

I.—*Variation of Size and Shape of Vessel.*

A series of sparks from the coil in normal working conditions was passed between "naked" platinum wire terminals (0·4 mm. diameter) about 5 mm. apart, the vessels being of the shape and dimensions stated in table I. If the mixture failed to ignite on sparking for about one second, more electrolytic gas was introduced, and the sparking test repeated. The limiting pressure of inflammability was taken as the mean between the lowest pressure of the gas in which a flame was produced and the highest pressure at which ignition had been impossible. These two pressures were never more than 2 mm. apart. The first three rows of the table contain the results obtained in three vessels made as nearly alike as possible, and indicate how closely the values can be reproduced.

TABLE I.

The vessel.			Ignition pressure with sparks from coil actuated with	
Description.	Length, in mm.	Internal diameter, in mm.	2 cells, in mm.	4 cells, in mm.
Cylinder, short narrow (i)	140	16	61	57
,, ,, ,, (ii) ...	140	16	—	54
,, ,, ,, (iii)	140	16	59	51
,, long, narrow	590	17	62	59
,, wide........................	240	36	60	58
Globe, small	—	49	61	57
,, large	—	81	56	54

Thus, within the limits of these experiments, a wide variation in the shape and size of the vessels employed had little influence on the ignition-pressure when the length of the spark gap was constant at 5 mm. The ignition-pressure was slightly but appreciably lowered in these experiments by the use of four accumulators instead of two. With another coil, the effect of four accumulators was more marked, the ignition-pressure being reduced some 30 to 40 per cent.

II.—*Variation in the Length of the Spark.*

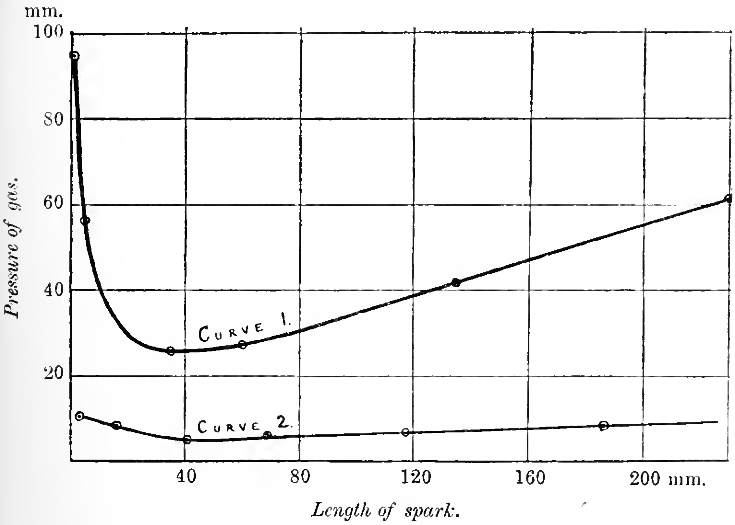
Since variation in the dimensions of the vessels produced little effect on the ignition-pressure, the results in several of the vessels may be compared to show the influence of varying length of spark-gap. For table II the results were obtained by exciting the coil with four cells and employing the trembler as usual; the electrodes were naked platinum wires as before.

TABLE II.

Vessel.	Length, in mm.	Diameter, in mm.	Ignition-pressures (in mm.) with spark gap of length						
			1 mm.	5 mm.	35 mm.	60 mm.	135 mm.	230 mm.	580 mm.
Cylinder	140	16	92	57	—	—	39	—	—
,,	140	16	118	54	—	—	44	—	—
,,	140	16	82	51	—	—	—	—	—
,,	590	17	89	59	—	—	—	—	above 126
,,	240	36	94	58	—	—	—	61	—
Globe ...	—	49	97	57	25·5	—	—	—	—
,, ...	—	81	90	54	—	27	—	—	—
	Mean		94·5	56	25·5	27	41·5	61	above 126

It is thus evident that the length of the spark-gap is of prime importance in determining the ignition of a gaseous mixture, in that the igniting power of the discharge increases with increasing length up to a maximum (about 35 mm. for the particular experimental arrangement in use), and then as the discharge becomes attenuated its igniting power diminishes.

FIG. 1.



The mean values are plotted in curve No. 1. Curve No. 2 shows a set of results all obtained in one globe with movable electrodes, by means of a stronger discharge produced as explained later.

Fresh samples of gas were used for each sparking test in these and in all the subsequent experiments.

III.—*The Igniting Power of a Single Spark.*

A single spark was obtained by screwing up the trembler on the induction coil, and introducing a break consisting of an amalgamated copper wire dipping into mercury. This procedure short-circuited the condenser of the coil so that the spark from the secondary could only jump a half-inch air-gap, instead of two inches as formerly. In spite of this, it proved to have much more igniting power, as shown by the following table:

TABLE III.

		Ignition-pressure with	
Vessel.	Spark gap, in mm.	Series of sparks, in mm.	Single spark, in mm.
Globe, 49 mm. diameter, naked platinum wire terminals.	1	97	8·5
	5	57	15
	35	25·5	12
Globe, 49 mm. diameter, glass covered terminals, pointed exposed lips.	1	57	29
	5	38·5	39
	35	28	17
Globe, 49 mm. diameter, glass covered terminals, flat exposed ends.	1	19	20
	5	17	9
	35	17	5·5

A second Ruhmkorff coil showed exactly the reverse effect, the single spark being less effective than a series obtained with the trembler.

IV.—*The Position of the Electrodes in a Cylindrical Tube.*

The Effect of Covering the Electrodes with Glass, so that only the Ends are Exposed.

Two cylindrical glass vessels of length 50 cm. and diameter 4·0 cm. were each provided with three pairs of electrodes. One of these pairs was near the top, the second in the middle, the third at the bottom of the tube. The electrodes in one vessel were glass-coated with the ends ground in order to expose only the flat tips of the wires. The electrodes in the other vessel were not so protected. The spark-gaps were all of 5 mm. length. The following results were obtained (new coil, 2 accumulators), three or four single sparks being employed for each trial.

TABLE IV.

Covered electrodes (in mm.).			Uncovered electrodes (in mm.).		
Upper.	Middle.	Lower.	Upper.	Middle.	Lower.
37, 34, 30	30, 25	40, 35, 40	77	60, 60	65
30, 28	—	—	72	70	68
32	35	40, 41, 38, 35	60, 55	58	65, 60, 58
33, 30, 37	25, 25	30	60, 55	50	50, 50
35	—	30	50	—	—
33	—	30	47	—	38
30	—	28	51	—	—
30	—	—	50	—	—
28	—	—	47	—	—
28	—	—	47	—	—
28	—	—	44	—	—
28	—	—	45	—	—
28	—	—	45	—	—
27	—	—	42	—	—

These results are tabulated in the order in which they were obtained, those in the same row being obtained on the same day. They show (i) that the covered electrodes produce a better igniting discharge than the uncovered ones; (ii) that there is little or no difference in igniting power of a discharge in electrolytic gas, whether it be produced at the top, bottom, or middle of the explosion tube; (iii) that the spark becomes more effective as the electrode is used. The reason must lie in a progressive change of the electrodes, perhaps due to disintegration. There was obviously much splashing of the platinum on to the glass in the neighbourhood of the electrodes.

V.—*Further Variation of the Character of the Electrodes.*

In order to discover whether a more powerful igniting discharge could be produced from the coil used with the same source of current for the primary, glass-coated electrodes exposing sometimes a drawn-out tip, sometimes an enlarged end (2 mm. diameter), were used. The vessels were glass globes of 49 mm. diameter. The results were:

TABLE V.

	Ignition-pressure (in mm.) with spark gap of length		
Electrodes.	1 mm.	5 mm.	35 mm.
Glass-covered, sharply pointed	29	39	17
,, enlarged plane ends...........	20	9	5·5
,, positive terminal pointed negative terminal plane	—	—	7·5
,, positive terminal plane negative terminal pointed	—	—	15

VI.—*Study of some other Factors.*

A bulb of 490 c.c. capacity with a spark-gap of 140 mm., the electrodes being glass-coated with enlarged ends, was used for the following tests.

A break consisting of a bluntly-pointed steel needle suspended from a spring and dipping into mercury when the spring was distended, gave an ignition-pressure of 7·5 mm. when the mercury was covered with alcohol, 10·5 when a heavy oil was used. After some time the oil became clouded with minute globules of mercury, and the efficiency of the spark was impaired.

When a small electromagnet was used to blow out the primary spark, exactly the same results were obtained with alcohol and oil respectively as above.

The introduction of an external air-gap of 22 mm. raised the ignition-pressure from 7·5 to 10·5 mm., an air-gap of 74 mm., to 17·5 mm.

Removal of the condenser attached to the primary break (the mercury break being now in place of the trembler) raised the ignition-pressure from 7·5 mm. to 9·5 mm.

VII.—*Is the Combustion of Electrolytic Gas Complete under Low Pressures?*

The ignition of electrolytic gas was always visible in a darkened room, even at the lowest pressures. The glass vessel was filled with a faintly blue flame, the propagation of which was too rapid to be followed by the eye. Even at 5 mm. it was quite distinct in size

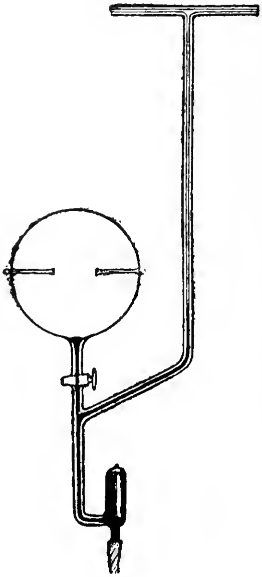
TABLE VI.

Pressure of gas ($2H_2+O_2$) in vessel before ignition.	Percentage of total gas unburnt.			Percentage unburnt × Initial pressure.			Thickness of layer of unburnt gas (in mm.).		
	Globe, 570 c.c.	Globe, 2720 c.c.	Cylinder, 3450 c.c.	Globe, 570 c.c.	Globe, 2720 c.c.	Cylinder, 3450 c.c.	Globe, 570 c.c.	Globe, 2720 c.c.	Cylinder, 3450 c.c.
70	0·10	—	—	7	—	—	0·017	—	—
50	0·14	—	—	7	—	—	0·024	—	—
40	0·18	0·20	0·43	7	8	17	0·031	0·058	0·049
30	0·32	0·26 0·25	0·37	10	8 7·5	11	0·054	0·075 0·072	0·043
20	0·43	0·35 0·31	1·35	9	7 6	27	0·073	0·102 0·090	0·16
15	0·53	—	—	8	—	—	0·090	—	—
12	0·65	—	3·1 2·7	8	—	37 32	0·11	—	0·36 0·31
10	1·15 1·02	0·65	—	11 10	6·5	—	0·19 0·17	0·19	—
8	—	—	5·5 4·8	—	—	44 38	—	—	0·63 0·55
7	1·14	0·92	—	8	6·5	-	0·19	0·27	—
5	1·4	—	—	7	—	—	0·23	—	—

and colour from the more localised glow which appeared when the discharge passed without causing ignition. Moreover, the discharge after ignition was red in colour, in sharp distinction from the colour of the discharge in electrolytic gas.

Such observations prove no more than that a portion of the mixture had inflamed, even with the additional evidence of the pressure gauge in use. It seemed a matter of some interest to inquire whether combustion was complete in this mixture; so the apparatus was modified to the form shown in Fig. 2. The globe was filled with gas at the required pressure, and mercury was passed into the capillary tube until it stood flush with the inner surface of the globe—so that the whole of the gas was contained in the globe, no gas being in side-tubes * where a flame might be extinguished. This caused no appreciable change in the pressure of the gas to be sparked. The connexions to the manometer and pump were then exhausted, the gas was ignited, the mercury run back to below the lower T-piece, and the residual water-vapour and gas were pumped out and collected. Such small amounts of gas were obtained that it was necessary to repeat each experiment many times in order to collect sufficient gas for measurement and analysis.

FIG. 2.



The results of a series of experiments with two globes of different sizes and one cylinder, 2 metres long, are shown in table VI. The last three columns of this table show the mean thickness of the layer of unburnt gas in each experiment, calculated on the assumptions (i) that the unburnt gas lies wholly on the walls of the vessel and of the electrodes, (ii) that the concentration of the gas in this layer is the same as in the bulk of the gas.

It is evident from the table:

(i) That for all three vessels the percentage of gas unburnt, and the thickness of unburnt layer deduced from this, increases as the pressure is diminished.

(ii) That for each of the two globes the following relation holds approximately:

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* This precaution is necessary in experiments at low pressures.

Percentage unburnt × initial pressure = constant; and therefore:

Thickness of unburnt layer × initial pressure = constant.

If this relation hold at atmospheric pressure, the amount of electrolytic gas unburnt would be of the order of 0·01 per cent., and would be distributed in a film the thickness of which is about 0·002 mm. These values do not refer to gases through which the explosion wave is passed. In this case some 1 per cent. of the mixture remains unburnt (H. B. Dixon and H. W. Smith, *Mem. Manchester Phil. Soc.*, 1889, [iv], **2**, 2).

(iii) That the larger globe shows a smaller percentage of unburnt gas at each pressure, but a greater thickness of the unburnt layer. The assumptions made in calculating this thickness are therefore incomplete; we suggest another: that the distance the flame has travelled from the spark has an influence upon the extent to which the film of gas next to the surface is penetrated by this flame. This cannot, however, be further tested by experiment in globes, and it is obvious from the table that the passage of a flame along a tube gives results which cannot be compared with those obtained in globes; in a tube the flame has an evident drag at the sides; in a globe the flame travels from the centre directly towards the sides. If the ignition is not at the centre of the globe, the flame assumes more or less the conditions of a flame in a tube.

VIII.—*The Minimum Ignition-pressure of Electrolytic Gas.*

The lowest ignition-pressure observed is 5 mm., which is considerably lower than any number previously recorded. In the largest globe ignition succeeded at 7 mm., and in the 2-metre tube a flame was seen to pass the whole length, upwards or downwards, at 8 mm. In this last case the flame travelled so far from the igniting discharge, and so slowly, that its continued propagation must have become independent of the initial aid of the spark. The flame was readily followed by the eye, and seemed only just able to pass along; a more intense discharge might have initiated a flame at a slightly lower pressure, but it seems improbable that the flame could have travelled far. At such pressures the loss of heat from the flame itself must be considerable. It seems, then, that the minimum ignition-pressure of a considerable amount of electrolytic gas, in the most favourable circumstances, is about 8 mm.

IX.—*The Erratic Results of De Hemptinne.*

We had no difficulty in repeating the values found in several forms of our apparatus, on separate occasions with intervals of a day or so, provided care was taken to keep all experimental circumstances constant. De Hemptinne obtained numbers in his apparatus varying erratically between 34 and 85 mm. This irregularity, he thought, might be due to a disturbance in the homogeneity of his mixture on passage from the gas-holder to the eudiometer tube. This seemed to us improbable, but we attempted to find such a change in composition by passing gas through about 2 metres of capillary tubing (2 mm. bore). The first and last portions were always of the same composition as the original gas. It is probable, therefore, that, as De Hemptinne suggested later, his electric discharge was the source of the trouble.

X.—*Summary.*

The minimum pressure at which electrolytic gas may be ignited by an electric discharge from a Ruhmkorff coil is independent of:

(i) the size and shape of the vessel employed, except at low pressures (5 to 10 mm.), or with very small vessels;

(ii) the position of the electrodes in the vessel.

It is lowered by the use of electrodes covered with glass but exposing their tips, preferably enlarged. It is sometimes raised, sometimes lowered, by the use of a single break in place of the trembler.

As the spark-gap increases in length, the ignition-pressure passes through a minimum.

A flame which filled a 570 c.c. globe has been produced at 5 mm. pressure; one which travelled through a cylinder of 2 metres length at 8 mm.

The residual gases have been examined, and the minute amount of gas remaining unburnt, due apparently to the cooling action of the walls of the vessel, estimated. In two globes the unburnt fraction of the gas varied inversely as the original pressure of the gas.

In the extraordinarily complicated character of the ignition of a gaseous mixture it is difficult to obtain data which may lead to a quantitative treatment of the subject. We hope to indicate soon a further advance made by a study of the relative ignition-pressures of various mixtures of gases, and later to show how the information obtained has been applied to explain the discrepancies in the values given by other observers for the dilution limits of inflammability.

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CCXL.—*Contributions to the Chemistry of the Terpenes. Part XIV. The Oxidation of Pinene with Hydrogen Peroxide.*

By George Gerald Henderson and Maggie Millen Jeffs Sutherland, B.Sc.

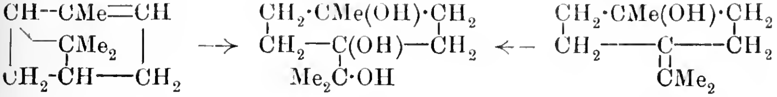
Having previously found that camphene is readily oxidised by hydrogen peroxide under suitable conditions (Trans., 1911, **99**, 1539), we proceeded to examine the action of this reagent on pinene in the hope of obtaining some simple derivatives, such as pinene glycol, containing a nucleus with the same structure as that of the parent hydrocarbon. This expectation was not realised; on the contrary, the results of our experiments illustrate once again the readiness with which the dimethyl*cyclo*butane ring in pinene undergoes disruption, as, for instance, under the influence of hydrogen chloride, of mercuric acetate, or of hydrating agents.

The chief product of the action of hydrogen peroxide on pinene, under the conditions described below, was found to be **α**-terpineol, $C_{10}H_{17}\cdot OH$, partly in the free state and partly in the form of an acetate. The other neutral products of the reaction included borneol, $C_{10}H_{19}\cdot OH$ (as an acetate), a small quantity of dipentene, a trace of the aldehyde of the formula $C_{10}H_{16}O$ which was originally obtained as a product of the action of chromyl chloride on pinene (Henderson and Gray, Trans., 1903, **83**, 1299), a little of a substance which appeared to be menthane-1:4:8-triol (trioxyterpan), $C_{10}H_{17}(OH)_3$, and some resinous matter. Neither pinene glycol nor any ketone could be detected, and only a very small quantity of an acid was produced. The products were therefore very different in character from those obtained by oxidising camphene under similar conditions (*loc. cit.*).

The conversion of pinene into terpineol under the influence of hydrating agents, and into esters of borneol by heating with organic acids, are well-known reactions. It is interesting to find that hydrogen peroxide effects the same transformations. The production of menthane-1:4:8-triol (II) from pinene (I) is obviously the result of simultaneous hydration and oxidation of the hydrocarbon, and may be represented by the equation:

$$C_{10}H_{16} + H_2O + H_2O_2 = C_{10}H_{17}(OH)_3.$$

This trihydric alcohol has already been obtained from $\Delta^{4(8)}$-menthenol-1 (III) by oxidation with dilute aqueous potassium permanganate (Baeyer and Blau, *Ber.*, 1895, **28**, 2296), but, so far as we are aware, its direct formation from pinene has not been recorded hitherto:



(I.) (II.) (III.)

The dipentene found among the products of the reaction was probably produced by dehydration of some of the terpineol, although the conditions were not such as to favour a reaction of this kind.

The action of hydrogen peroxide on other terpenes is at present under investigation.

EXPERIMENTAL.

The pinene used in our experiments was prepared from American oil of turpentine by a process which according to our experience yields a practically pure product. The oil of turpentine, after agitation with aqueous sodium carbonate, was distilled in a current of steam until about two-thirds of the oil had passed over, and this fraction was again treated in a similar manner. The distillate was separated from the condensed water, dried with sodium hydroxide, and fractionated with the aid of a "pear" still-head, the portion which boiled at 155—156° being taken as pinene. A series of experiments which we have carried out, and of which it is unnecessary to give details, have established the fact that the separation of pinene from oil of turpentine is greatly facilitated by fractional steam distillation of the oil, because the pinene volatilises more readily in a current of steam than the other hydrocarbons which appear to be always present, although in variable proportions, in oil of turpentine.

In order to effect the oxidation, the necessary quantity of a 30 per cent. aqueous solution of hydrogen peroxide was added to a solution of pinene in glacial acetic acid (about 250 grams of solvent for 100 grams of pinene), and the mixture heated on a water-bath at 40—60° until the pinene, which separated on addition of the hydrogen peroxide, had again passed into solution. Under these conditions the oxidation proceeds very slowly, but attempts to hasten the process by carrying it out at higher temperatures resulted in the formation of much resinous matter. The best results were obtained when two molecular proportions of hydrogen peroxide were added to one of pinene.

When the oxidation of the pinene was completed, the solution was diluted with water, the acetic acid almost neutralised by addition of sodium carbonate, and the oily product, which had separated, extracted by means of ether. The ethereal solution was washed and dried, the ether distilled off, and the residual oil warmed with aqueous sodium carbonate in order to remove any acids which it contained. After cooling, the undissolved neutral products were separated from the alkaline solution by means of ether.

From the alkaline solution, by acidification and extraction with ether, a very small quantity of an acid, or mixture of acids, was obtained in the form of a brown, syrupy liquid. This was not further examined.

The ethereal solution of the neutral oxidation products was washed and dried, the ether removed, and the oily residue mixed with a saturated solution of sodium hydrogen sulphite. After several days a small quantity of crystals of a bisulphite compound was deposited. The oil, which for the most part remained undissolved, was removed by shaking the mixture with ether, and the aqueous solution was then mixed with sodium carbonate and distilled in a current of steam. A small quantity of an aldehyde came over as a soft, crystalline mass, and in its appearance and peculiar odour was exactly similar to the aldehyde $C_{10}H_{16}O$ formerly obtained as a product of the oxidation of pinene with chromyl chloride. As the quantity was too small to permit of satisfactory analysis, the aldehyde was converted into a semicarbazone in the usual manner. The semicarbazone, after recrystallisation from methyl alcohol, melted at 190—191°, and a mixture of this with the semicarbazone of the aldehyde, $C_{10}H_{16}O$ (m. p. 191°), melted at the same temperature.

After removal of the aldehyde, the mixture of neutral oxidation products was distilled in a current of steam. The greater part volatilised readily, but a portion remained in the distillation flask. The volatile part was separated from the condensed water by means of ether, and the oil which remained on evaporation of the ether was distilled under diminished pressure, and after several fractionations separated into three distinct parts. The fraction of lowest boiling point, of which the quantity was very small, proved to be unchanged pinene. The second fraction, which was larger in amount, boiled at 62—64°/16 mm., and the principal fraction boiled at about 100—104°/16 mm. This last fraction, which at first was supposed to be composed of one substance because no separation took place on further fractionation, had a strong odour somewhat like that of terpineol, and a small portion, when left in contact with very dilute sulphuric acid for a considerable time, yielded some crystals of terpin hydrate. The bulk of the fraction was cooled in a freezing mixture, seeded with some particles of α-terpineol (m. p. 35°), and stirred. A crystalline solid gradually separated, which was collected. The portion which remained liquid was repeatedly subjected to the same treatment until no further separation of crystals could be brought about. The crystalline portion melted, after purification, at 35°, and had the other physical properties of α-terpineol. In order to complete the identification, we prepared its phenylurethane, colourless crystals melting sharply at 113°, and its nitrosochloride, small, colourless needles which melted at 122°, and finally converted a portion into terpin hydrate, m. p. 120°, by agitation with 5 per cent. sulphuric acid.

After the terpineol which it contained had been separated, as completely as possible, from the fraction of b. p. 100—104°, the oil which remained was hydrolysed by heating for some time with methyl-alcoholic potassium hydroxide under a reflux condenser. The alcohol was then distilled off, and the residue mixed with water and thoroughly extracted with ether. Examination of the alkaline solution revealed the presence of acetic acid alone. The ethereal solution was washed with water and dried with anhydrous sodium sulphate, and the oil which remained on evaporation of the ether was distilled under diminished pressure. Almost the whole passed over at 99—101°/16 mm., a very small quantity at a higher temperature. When cooled in a freezing mixture the distillate yielded a further quantity of terpineol, but a portion could not be induced to solidify, and on redistillation was found to boil at 95—99°/16 mm. Five grams of this oil were mixed with an equal weight of phthalic anhydride and heated at 110° for four hours. The mixture was then poured on crushed ice, and stirred with the necessary quantity of aqueous sodium carbonate until the ester had passed into solution. After removal of excess of phthalic anhydride by filtration, the aqueous filtrate was found to be mixed with a quantity of an oily liquid. This liquid was separated by means of ether, and ultimately proved to be dipentene, by analysis and by its conversion into the characteristic tetrabromide. The aqueous filtrate was acidified and agitated with ether, the ethereal solution washed and dried, the ether removed, the residue digested with chloroform, and the phthalic acid, which is practically insoluble in that solvent, removed by filtration. On evaporation of the chloroform the ester was left in a viscid condition, and could not easily be purified from a little of a yellow substance with which it was mixed, but finally was obtained in glistening, colourless plates by crystallisation from a mixture of ether and light petroleum. It melted at 155°, was very readily soluble in ether or alcohol, but sparingly so in light petroleum. Analysis gave results which agreed with those calculated for the hydrogen phthalate of an alcohol of the formula $C_{10}H_{18}O$. (Found, C=71·4; H=6·7. $C_{18}H_{22}O_4$ requires C=71·5; H=7·3 per cent.)

The ester was hydrolysed on the water-bath with the necessary quantity of aqueous sodium hydroxide, and, after cooling, the solid alcohol which had separated was collected and purified by distillation in a current of steam and crystallisation from light petroleum. It crystallises in colourless plates, which melt at 203° in a closed tube and sublime readily, and has the odour of borneol. A mixture of the alcohol with borneol also melted at 203°; there can be no doubt as to its identity.

In order to prove that the ester was not by any chance derived from terpineol under the conditions of its preparation, some terpineol was heated for a few hours at 110° with the calculated quantity of phthalic anhydride. Practically no ester was formed, but there was a large yield of dipentene, the phthalic anhydride in this as in other cases having acted as a dehydrating agent. In this way also the presence of dipentene in the product obtained by heating the oily impure borneol with phthalic anhydride was accounted for, the alcohol having been mixed with some terpineol which could not be separated by cooling. Experiment also showed that terpineol and borneol readily form a liquid mixture.

The fraction of the neutral oxidation products which boiled at 62—64°/16 mm. was analysed, with results which pointed to the conclusion that it was chiefly composed of a hydrocarbon, $C_{10}H_{16}$. As it was found to be unsaturated, a bromide was prepared by gradual addition of a slight excess of bromine dissolved in dry chloroform to a cooled solution of the oil in the same solvent. On evaporation of the chloroform under diminished pressure the bromide was left as a crystalline mass, which was drained on a porous plate and purified by crystallisation from alcohol. It separates in lustrous plates, is sparingly soluble in ether and in cold alcohol, but readily so in hot alcohol, and melts sharply at 125°. Analysis showed its formula to be $C_{10}H_{16}Br_4$. (Found, Br=70·1. Calc., Br=70·2 per cent.) Its melting point agrees with that of dipentene tetrabromide, and a mixture of the two compounds melted at the same temperature. The presence of dipentene among the products of the action of hydrogen peroxide on pinene is therefore proved.

The portion of the neutral oxidation products which did not volatilise in a current of steam was found to be partly soluble and partly insoluble in water and was therefore repeatedly stirred with warm water until nothing more passed into solution. The insoluble portion appeared to be mostly composed of resinous matter, and was not further examined. The aqueous solution was saturated with ammonium sulphate and repeatedly agitated with ether, the ethereal solution dried with anhydrous sodium sulphate, and the residue left on evaporation of the ether distilled under diminished pressure. Owing to the extremely viscous nature of the substance, fractionation was difficult, and no very definite separation was effected; in addition, there was a slight amount of decomposition. Ultimately, however, the bulk of the product was obtained as a very viscous liquid, which boiled at 150—170°/16 mm., whilst a small portion passed over above 170°. When mixed with a little benzene, cooled in a freezing mixture, and stirred, a considerable part of the distillate gradually assumed the crystalline form. The crystals were collected, drained on a porous plate, and purified by crystallisation from benzene. The substance was thus obtained in minute, colourless needles, which melted at 110—111°. It is readily soluble in water, alcohol, or hot benzene, sparingly so in cold benzene or ether. From water it crystallises in the hydrated form, which melts at 95—96°. Analysis pointed to the formula $C_{10}H_{20}O_3$. (Found, C = 63·4; H = 11·3. Calc., C = 63·8; H = 10·6 per cent.) The compound is saturated, and when distilled with very dilute sulphuric acid it yields a substance which readily unites with bromine. In all these respects the compound is identical with menthane-1:4:8-triol (trioxyterpan).

The small fraction which distilled above 170° when mixed with methyl alcohol yielded a little of a colourless, crystalline compound. After purification by crystallisation from methyl alcohol this substance melted at 55—56°. It is readily soluble in ether, but sparingly so in methyl alcohol, and, as it is insoluble in water, must probably have been formed during the distillation process. The quantity was too small to admit of fuller examination.

We are indebted to the Research Fund Committee of the Carnegie Trust for a grant which defrayed the expense of this work.

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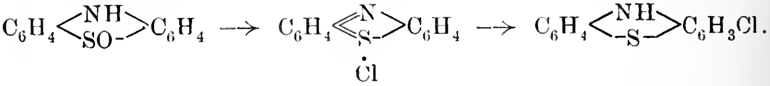
CCXLI.—*The Intramolecular Rearrangement of Diphenylamine* ortho-*Sulphoxides. Part IV.*

By Thomas Percy Hilditch and Samuel Smiles.

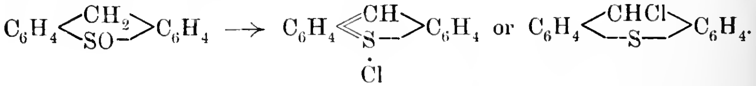
The experiments which form the subject of the present communication were made in continuing the study of the intramolecular changes which the *o*-sulphoxides of diphenylamine undergo on treatment with acids. As the result of previous experiments (Trans., 1909, **95**, 1253; 1910, **97**, 186, 1112, 1559), it was shown that the interaction of cold concentrated hydrochloric acid and the *o*-sulphoxide of diphenylamine yields phenazothionium chloride, whilst with the hot reagent the latter substance is converted into chlorothiodiphenylamine:



$$C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{SO}{>}C_6H_4 \longrightarrow C_6H_4{\ll}\genfrac{}{}{0pt}{}{N}{\underset{\displaystyle Cl}{S}}{>}C_6H_4 \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{S}{>}C_6H_3Cl.$$

The ease with which the transformation of the sulphoxide is effected depends on the strength of the acid employed; thus, whilst trichloroacetic acid acts energetically, monochloroacetic acid is almost without influence at the atmospheric temperature.

With the *o*-sulphoxide of diphenylmethane cold hydrochloric acid readily gives (Trans., 1911, **99**, 145) the analogous carbothionium salt, and if the excess of the mineral acid is removed, thioxanthenyl chloride is obtained:



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH_2}{SO}{>}C_6H_4 \longrightarrow C_6H_4{\ll}\genfrac{}{}{0pt}{}{CH}{\underset{\displaystyle Cl}{S}}{>}C_6H_4 \text{ or } C_6H_4{<}\genfrac{}{}{0pt}{}{CHCl}{S}{>}C_6H_4.$$

Moreover, with weaker acids, such as warm glacial acetic acid, this sulphoxide furnishes thioxanthenol.

This occurrence of thioxanthenyl chloride and of thioxanthenol necessitated a search for the corresponding derivatives of thiodiphenylamine in the reacting mixtures of the sulphoxides of that series with hydrochloric acid; for it is clear that, should the occurrence of *N*-chloro-derivatives therein be demonstrable, important evidence on the mechanism of the change would be at hand. However, the previous work of Armstrong, of Chattaway, and especially that of Orton on the nature of *N*-chloro-compounds, permits but slight hope of isolating these substances from mixtures containing an excess of hydrogen chloride; hence experiments in this direction were confined to the tetrachlorodiphenylamine sulphoxide, the *N*-chloro-derivative of which might be expected to be somewhat more stable than those of the less substituted analogues; but the results were negative. Attention was therefore turned to the question whether these sulphoxides would yield the oximino-compounds or their derivatives if weak acids, such as acetic, were employed in effecting the rearrangement.

In the present experiments it is shown that the rearrangement of the sulphoxides of diphenylamine may, indeed, be effected with acetic acid; but the oximino-compounds in request could not be found in the product; in fact, the unsubstituted sulphoxides of this series when heated with glacial acetic acid yield the hydroxy-derivatives of the nucleus, in contrast to the behaviour of the *o*-sulphoxide of diphenylmethane which furnishes thioxanthenol under similar treatment:

$$C_6H_4{<}\substack{NH\\SO}{>}C_6H_4 \longrightarrow C_6H_4{<}\substack{NH\\S}{>}C_6H_3\cdot OH.$$

It may be remarked that the phenazothionium phase observed when hydrogen chloride is used as the reagent has not been detected in this or similar cases where the aromatic nuclei are unsubstituted. The behaviour of three typical members of the series has been examined: the *o*-sulphoxides of diphenylamine, diphenylmethylamine, and of tetrachlorodiphenylamine. As might be expected, the last-named substance behaves exceptionally, for, the nuclei being fully substituted, the interaction proceeds no further than to the phenazothionium hydroxide, which appears to be a relatively stable substance.

The interaction of excess of acetic acid and these sulphoxides is barely perceptible even after prolonged treatment at the atmospheric temperature, but it may be carried out by heating the reagents at 140° for three or four hours in sealed vessels.

EXPERIMENTAL.

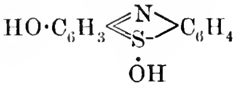
Diphenylamine o-*Sulphoxide.*

Reaction with acetic acid was effected as mentioned. The product was a purple, crystalline mass, sparingly soluble in cold glacial acetic acid; but since attempts at purification by the usual methods did not give definite results, other means were adopted for determining the nature of the substance. It was submitted to treatment with zinc dust and hot acetic acid, when reduction took place, and on pouring the filtered liquid into excess of cold water a colourless, crystalline substance was obtained. This was purified by recrystallisation from dilute methyl alcohol, when *hydroxythiodiphenylamine* was isolated in soft, white crystals, which rapidly became purple in presence of air:

0·1304 gave 0·3190 CO_2 and 0·0520 H_2O. C=66·73; H=4·4.

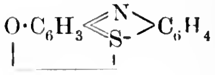
$C_{12}H_9ONS$ requires C=67·0; H=4·19 per cent.

In order to confirm the conclusion formed from the analytical data and properties, the substance was oxidised in acid alcoholic solution with ferric chloride. The recrystallised product was deep brown, and analysis showed that it was hydroxyphenazothionium



$HO\cdot C_6H_3 < \genfrac{}{}{0pt}{}{N}{\underset{\dot{O}H}{S}} > C_6H_4$

(I.)



$\underbrace{O\cdot C_6H_3 < \genfrac{}{}{0pt}{}{N}{S}}\, > C_6H_4$

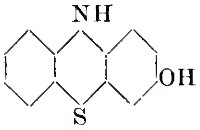
(II.)

hydroxide (I), the anhydride of which—phenazothion (II)—has been previously observed by Kehrmann (*Annalen*, 1902, **322**, 1):

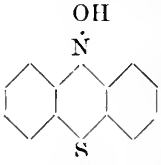
0·1160 gave 0·2638 CO_2 and 0·0428 H_2O. C=62·0; H=4·1.

$C_{12}H_9O_2NS$ requires C=62·3; H=3·9 per cent.

These data show that the main product of interaction between acetic acid and the *o*-sulphoxide of diphenylamine is the hydroxy-derivative of thiodiphenylamine (III), and not the oximino-deriv-



(III.)



(IV.)

ative (IV), for, were it the latter, reduction should furnish thiodiphenylamine.

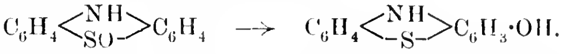
Similar results were obtained with the *o*-sulphoxide of diphenylmethylamine. In this case the product of interaction with acetic acid, obtained under the stated conditions, contained a small quantity of an insoluble purplish-black substance of high melting point; this was not further investigated, attention being confined to the more soluble portion which composed the greater part of the product of reaction. This substance, as in the previous case, defied attempts at direct resolution into a pure substance, but reduction with zinc dust and acetic acid and repeated crystallisation of the product from dilute alcohol yielded an almost colourless, crystalline substance, which melted somewhat indefinitely at 128°. This was readily oxidised by exposure to air or by ferric chloride, a purplish-brown material being formed.

Analysis showed that the substance was *hydroxythiodiphenylmethylamine*:

0·1688 gave 0·4258 CO_2 and 0·0786 H_2O. C=68·79; H=5·1.

$C_{13}H_{11}OSN$ requires C=68·13; H=4·8 per cent.

From the foregoing results there can be no doubt that these sulphoxides when heated in acetic acid solution undergo the change expressed by the following formulæ:



$$C_6H_4<\genfrac{}{}{0pt}{}{NH}{SO}>C_6H_4 \longrightarrow C_6H_4<\genfrac{}{}{0pt}{}{NH}{-S-}>C_6H_3\cdot OH.$$

At the same time it may be observed that the material actually isolated evidently is not the pure hydroxy-derivative which is represented, but is a partly oxidised form thereof. The instability of these hydroxy-derivatives in presence of air at the high temperature employed in the interaction is well known, and the pure substances could not be expected.

It appears, nevertheless, that the foregoing results do not permit the rigid conclusion that the oximino-derivatives are not formed, for, in view of the experiments made by Bamberger (see especially *Annalen*, 1912, **399**, 131) with phenylhydroxylamine, and the experience met with by Wieland and Gambarjan (*Ber.*, 1906, **39**, 1499) in their attempts to obtain diphenylhydroxylamine, it is possible that the substances now in request might be unstable, and tend to yield the phenolic compounds by intramolecular rearrangement.

Hence in order to reduce as far as possible this tendency to substitution in the aromatic nuclei, experiments were made with the *o*-sulphoxide of tetrachlorodiphenylamine, which is obtained by the exhaustive chlorination of thiodiphenylamine.

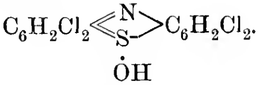
o-*Sulphoxide of Tetrachlorothiodiphenylamine.*

The interaction was effected under the conditions which were adopted in dealing with the foregoing sulphoxides. On cooling the reacting mixture a portion of the product separated from the liquid in chocolate-coloured needles. These were collected, and, after recrystallisation and drying in a vacuum over alkali hydroxide, were analysed:

0·1094 gave 0·1614 CO_2 and 0·0165 H_2O. C=40·4; H=1·68.

$C_{12}H_5ONCl_4S$ requires C=40·8; H=1·4 per cent.

The substance was identified in the usual manner as *tetrachlorophenazothionium hydroxide*:



$$C_6H_2Cl_2\ll\genfrac{}{}{0pt}{}{N}{\underset{\dot{O}H}{S-}}>C_6H_2Cl_2.$$

On examining the mother liquor a further quantity of this substance was obtained; in fact, no other compound could be isolated, the conversion of the sulphoxide into sulphonium base being apparently quantitative.

Similar results were obtained in studying the influence of mineral acids on tetra-substituted sulphoxides of this group. In previous papers (Trans., 1909, **95**, 1253; 1910, **97**, 1062) the behaviour of the tetranitro- and tetrachloro-sulphoxides has been recorded, and on repeating these experiments with hydrogen chloride as the reagent, special search was made for the chloro-imino-derivatives among the products of reaction, but these could not be detected, the phenazothionium hydroxides being the sole products.

In summarising these results it may be said that the action of heat on the unsubstituted sulphoxides of diphenylamine leads finally to the production of hydroxy-derivatives of the nucleus; but with sulphoxides of this group, in which the aromatic nuclei are highly substituted, the interaction remains at the phenazothionium derivatives. In contrast, the behaviour of the *o*-sulphoxide of diphenylmethane (Trans., 1911, **99**, 145) is noteworthy, for here the thionylic oxygen may be transferred by the action of heat to the *meso*-carbon atom, whilst from the experiments now recorded it seems improbable that a similar transference to nitrogen takes place in the thiodiphenylamine series.

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CCXLII.—*Studies in the Diphenyl Series. Part II. The Dinitrobenzidines: a New Form of Isomerism.*

By JOHN CANNELL CAIN, ALBERT COULTHARD, and
FRANCES MARY GORE MICKLETHWAIT.

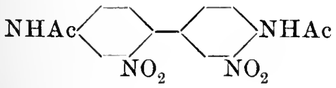
IN 1872 Strakosch (*Ber.*, **5**, 236) nitrated diacetylbenzidine and obtained a dinitrobenzidine, which was shown very conclusively by Brunner and Witt (*Ber.*, 1887, **20**, 1023) to contain the nitro-groups in the ortho-position with respect to the amino-groups.

On the other hand, Bandrowski (*Ber.*, 1884, **17**, 1181; *Monatsh.*, 1887, **8**, 472) by the nitration of diphthalylbenzidine obtained two dinitrobenzidines, one melting at 218—221°, and the other, "*iso*dinitrobenzidine," melting at 196—197°. Bandrowski, comparing the former with Strakosch's dinitrobenzidine, points out the distinct differences between them, the one being stated by Strakosch to melt at above 300° and to sublime at a higher temperature, and the other, discovered by Bandrowski, being found to melt at 218—221° and to inflame when heated further.

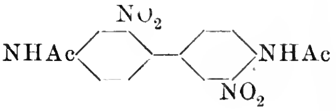
Bandrowski concluded that it appeared probable that his dinitrobenzidine was identical with that described by Strakosch, but pointed out that the identity could only be established by a direct comparison of the two substances. In spite of this guarded statement it has been assumed in the literature that the two compounds are identical, and the melting point 218—221° has been assigned to both.

As regards Bandrowski's "*iso*dinitrobenzidine," the elucidation of the constitution of this substance was really the original object of the present investigation, for, in view of the fact that both 3:3′- and 2:2′-dinitrobenzidine (Täuber, *Ber.*, 1890, **23**, 794) are described in the literature, the possibility of the formation of a third symmetrical dinitrobenzidine (and it would be difficult to imagine that an unsymmetrical one could be produced in the nitration process) seemed, in the present state of our knowledge, questionable.

Having, however, prepared a considerable amount of what may be termed Strakosch's dinitrobenzidine, following the directions of Brunner and Witt, for the purpose of another investigation, we naturally compared this substance with the chief product obtained in the nitration of diphthalylbenzidine, namely, Bandrowski's dinitrobenzidine, expecting to find, as suggested by the latter author, that the two were identical. It was soon suspected that they were not; and a careful comparison has shown that there exist two distinct ortho-dinitrobenzidines. Sufficient proof was furnished by Brunner and Witt that their product was a diortho-compound, and we have confirmed this by finding that on oxidation with potassium permanganate the diacetyl derivative yields 3-nitro-4-acetylaminobenzoic acid. No conclusive evidence has yet been adduced that Bandrowski's product was a diortho-compound, but we have proved that it has this constitution as follows: On oxidising its diacetyl derivative as above, 3-nitro-4-acetylaminobenzoic acid alone was obtained; this might conceivably have been produced by the oxidation of an unsymmetrical dinitrodiacetylbenzidine of the formula:



or

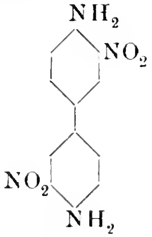


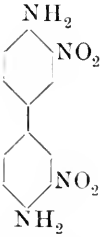
the ring containing the nitro- and amino-groups in the meta-position with respect to each other having been completely oxidised. The formation of such a compound by the nitration of a diacyl derivative of benzidine is, however, very improbable, but in order to place the matter beyond doubt the dinitrobenzidine was reduced to tetra-aminodiphenyl, and this, when condensed with benzil, the corresponding diquinoxaline, the formation of which proves that the dinitrobenzidine is a diortho-derivative.

The chief differences between the two dinitrobenzidines are as follows: Strakosch's dinitrobenzidine, prepared from diacetylbenzidine, crystallises in scarlet needles melting at 275°, is practically insoluble in water, yields a diacetyl derivative melting at 310°, and a dinitrodiphenyl melting at 197—198° (Brunner and Witt). Bandrowski's dinitrobenzidine, prepared from diphthalylbenzidine, crystallises in bright red, feathery needles (yellower than the preceding) melting at 233°, is appreciably soluble in water, yields a diacetyl derivative melting at 222° (Bandrowski gives "above 300°"), and a *dinitrodiphenyl* melting at 110°. Corresponding members of the two series, namely, the dinitrobenzidines, their diacetyl derivatives, and the dinitrodiphenyls, depress each other's melting point.

Both dinitrobenzidines, however, give on reduction and condensation of the product with benzil the same diquinoxaline, so that it would appear that the cause of the new isomerism may lie in some special property of the nitro-groups.

From these facts it seems justifiable to draw the conclusion that the constitutions of the two dinitrobenzidines must be represented by the formulæ:

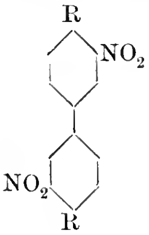




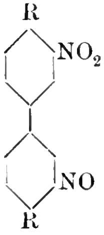
and this is, so far as the authors are aware, the first instance of such isomerism in the case of substances where the possibility of rotation of two carbon atoms about their common linking exists, although Willgerodt (*J. pr. Chem.*, 1888, [ii], **37**, 449; Willgerodt and Schultz, *ibid.*, 1891, [ii], **43**, 177) and Young and Annable (Trans., 1897, **71**, 204) have suggested that in certain compounds containing two nitrogen atoms linked together a similar isomerism is found, thus:

In this connexion it is of interest to recall that Täuber first assigned the 2:6′-constitution to *m*-dinitrobenzidine, but later proved that the nitro-groups were in the 2:2′-position, thus recognising the possibility of the isomerism, of which the above *o*-dinitrobenzidines, their diacetyl derivatives, and the corresponding dinitrodiphenyls appear to be examples.

It will be noticed that Strakosch's dinitrobenzidine, its diacetyl derivative, and the corresponding dinitrodiphenyl all melt at a considerably higher temperature than Bandrowski's product and the corresponding compounds prepared from it, and in view of the fairly general rule that symmetrical compounds have higher melting points than unsymmetrical, we suggest that, in the absence of any direct chemical evidence, the former compounds have the symmetrical constitution (I) and the latter the unsymmetrical constitution (II) (where $R = H$, NH_2, or NHAc):



(I.)



(II.)

It still remains to explain the nature of Bandrowski's "*iso*dinitrobenzidine." This was found not to be a single substance, but simply a mixture of 2:2′-dinitrobenzidine and 3:3′-dinitrobenzidine (m. p. 233°) with possibly a little 3-nitrobenzidine. The nitration of diphthalylbenzidine thus furnishes a mixture of 3:3′-dinitrobenzidine (m. p. 233°) with a small amount of 2:2′-dinitrobenzidine, a fact which is interesting in view of the circumstance that on nitration of diacetylbenzidine the nitro-groups assume the ortho-position, and in the case of benzidine sulphate the meta-position with respect to the amino-groups.

EXPERIMENTAL.

3:5′-*Dinitrobenzidine.*

Brunner and Witt's directions for preparing this compound were closely followed. The substance was obtained in the pure state (Found, $N = 20{\cdot}4$. Calc., $N = 20{\cdot}4$ per cent.) by crystallisation from phenol as recommended by these authors, and forms scarlet needles melting at 275°. This melting point is lowered when the substance is mixed with 3:3′-dinitrobenzidine.

One hundred c.c. of a boiling aqueous solution contained only 0·012 gram of the substance.

Strakosch (*loc. cit.*) noticed that a second product, crystallising in red needles, was obtained in the nitration of diacetylbenzidine, but he did not investigate it further. This second product consists of the isomeric 3:3′-dinitrobenzidine (see below), and is obtained from the crude substance by treatment with alcohol or concentrated hydrochloric acid. In the latter case the red needles which crystallise on cooling the solution are removed, and the filtrate is treated with water or ammonia, when 3:3′-dinitrobenzidine is obtained.

3:5′-Dinitrodiacetylbenzidine melts at 310°, a melting point which is lowered by mixing the substance with 3:3′-dinitrodiacetylbenzidine; when oxidised with potassium permanganate the diacetyl compound gives 3-nitro-4-acetylaminobenzoic acid.

When the dinitrobenzidine is reduced as described by Brunner and Witt to the tetra-aminodiphenyl and this condensed with benzil, the diquinoxaline produced melts at 299—300° (Brunner and Witt give "not at 275°").

3:3′-*Dinitrobenzidine.*

Diphthalylbenzidine was nitrated as described by Bandrowski. The crude product melted at 220—225° after softening at 218°, and after purification by crystallisation from alcohol, phenol, or water, or when obtained through the hydrochloride, formed red, feathery needles, melting at 233°. The pure material was subjected to various processes in order to prove that it was a single substance; thus it was fractionally crystallised from water, in which, unlike 3:5′-dinitrobenzidine, it is sparingly soluble (100 c.c. of a boiling aqueous solution contained 0·146 gram of the substance), but all the fractions melted at the same temperature. Fractional crystallisation from alcohol and fractional treatment with both dilute and concentrated hydrochloric acid also failed to produce any difference in the melting points of the various fractions.

In order to elucidate its constitution the diacetyl derivative, which is not identical with that described by Strakosch, and separates from glacial acetic acid in yellow, granular crystals melting at 222° (Bandrowski gives "above 300°"), was dissolved in glacial acetic acid, and aqueous potassium permanganate added until no further decolorisation occurred, the temperature being kept at about 60°. After filtering, the solution was neutralised with sodium carbonate, filtered from a little unchanged substance, and the cold filtrate acidified with hydrochloric acid. Extraction of this solution with ether furnished a pale yellow acid melting at 218—219°; this was mixed with 3-nitro-4-acetylaminobenzoic acid

(m. p. 219°; prepared by oxidising 3-nitro-4-acetotoluidide with potassium permanganate in the presence of magnesium sulphate) when the mixture melted at 219°. This result proves at least that the nitro- and amino-groups in one-half of the molecule are in the ortho-position with respect to each other, but in order to show that this is true of both rings the dinitrobenzidine was reduced to tetra-aminodiphenyl, the acetate of which was condensed with benzil. The diquinoxaline which was formed (Found, N = 10·5. $C_{40}H_{26}N_4$ requires N = 10·0 per cent.) melted at 299—300°, and a mixture of this with the diquinoxaline * prepared from Strakosch's dinitrobenzidine melted at the same temperature. Bandrowski's dinitrobenzidine is therefore a diortho-compound.

3:3′-*Dinitrodiphenyl.*

The two dinitrobenzidines described above were diazotised as directed by Brunner and Witt, and the bisdiazo-compounds were boiled with alcohol. Whereas Strakosch's dinitrobenzidine yielded the dinitrodiphenyl obtained by Brunner and Witt (now to be termed 3:5′-), Bandrowski's dinitrobenzidine gave a different *dinitrodiphenyl* (3:3′), which crystallises from glacial acetic acid in small, pale yellow needles melting at 110°, a melting point which could not be raised either by recrystallisation of the substance or by distillation under diminished pressure, but which is lowered when the substance is mixed with a little 3:5′-dinitrodiphenyl:

0·0654 gave 6·4 c.c. N_2 at 9° and 746·4 mm. N = 11·6.
$C_{12}H_8O_4N_2$ requires N = 11·5 per cent.

Bandrowski's "iso*Dinitrobenzidine.*"

When the product of nitration of diphthalylbenzidine is poured into water, a precipitate of 3:3′-dinitrobenzidine (m. p. 233°) is obtained. The filtrate, on neutralisation with ammonia, gives a precipitate which was purified by Bandrowski by extracting with dilute hydrochloric acid (in which his *o*-dinitrobenzidine is sparingly soluble), and precipitating the filtrate with ammonia. The substance obtained in this way was regarded by Bandrowski as an isomeric dinitrobenzidine, and he found it to melt at 197°. In repeating this purification instead of immediately precipitating the filtrate from extraction with dilute hydrochloric acid with ammonia, the filtrate was allowed to remain overnight, when it was found that a further quantity of 3:3′-dinitrobenzidine (m. p. 233°) had

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* The diquinoxaline prepared by Brunner and Witt, although described in 1887 is not mentioned in the new edition of Richter's *Lexikon.*

separated. The filtrate from this, on neutralisation with ammonia, gave a bright yellow base, which was boiled with insufficient 75 per cent. alcohol to dissolve the whole. (Residue = *A*.) The solution yielded slightly brownish-yellow needles melting at 210—212°, which on recrystallisation from absolute alcohol gave yellow needles melting at 214°, and these were proved to be 2 : 2′-dinitrobenzidine by a mixed melting-point determination. The filtrate from the brownish-yellow needles deposited a small amount of red needles melting at 188—189°. The quantity of these was too small for analysis, but they consisted apparently of 3-nitrobenzidine, the melting point of which is given as 190° (Koller, *Ber.*, 1904, **37**, 2880).

The residue *A* (see above) was dissolved in absolute alcohol, and from the solution there separated yellow needles melting at 214°, which were identified as 2 : 2′-dinitrobenzidine.

Bandrowski's "*iso*dinitrobenzidine" is thus shown to consist of a mixture of 3 : 3′-dinitrobenzidine (m. p. 233°), 2 : 2′-dinitrobenzidine, and probably a little of the 3-mononitro-compound.

An examination has also been made of the compound isolated by Cain and May (Trans., 1910, **97**, 724) in the preparation of 2 : 2′-dinitrobenzidine, which, it was suggested, might be identical with Bandrowski's *iso*dinitrobenzidine. This, on recrystallisation, gave 2 : 2′-dinitrobenzidine, and the filtrate contained probably a trace of 2-nitrobenzidine, the melting point of which is given as 143° (Täuber).

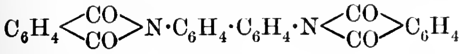
Further experiments on the isomeric *o*-dinitrobenzidines are in progress, and a search will be made for other examples of this isomerism among diphenyl derivatives, as the constitution of many of those described in the literature is yet unknown.

The expenses of this work have been partly defrayed by a grant from the Research Fund of the Chemical Society, for which the authors desire to express their grateful thanks.

CCXLIII.—*Studies in the Diphenyl Series. Part III. Diphenyldiphthalamic Acids and Pyronine Colouring Matters containing the Diphenyl Group.*

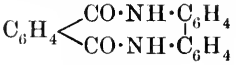
By John Cannell Cain and Oscar Lisle Brady.

It was shown by Bandrowski (*Ber.*, 1884, **17**, 1181; compare also Schiff, *ibid.*, 1878, **11**, 830) that when benzidine and phthalic anhydride are heated together at about 160—200° diphthalylbenzidine (I) is formed. If the materials are boiled together in aqueous suspension, however, the monophthalyl derivative (II)



$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>N\cdot C_6H_4\cdot C_6H_4\cdot N\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_4$$

(I.)



$$C_6H_4\left<\begin{matrix}CO\cdot NH\cdot C_6H_4\\ \vert \\ CO\cdot NH\cdot C_6H_4\end{matrix}\right.$$

(II.)

is produced (Koller, *Ber.*, 1904, **37**, 2880). The present authors have found that when the interaction is allowed to proceed at 100° for an hour in the presence of nitrobenzene, *diphenyl*-4:4′-*diphthalamic acid* (III) is obtained in quantitative yield,

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H.$$

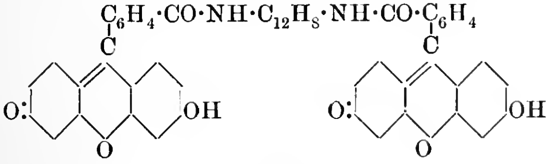
(III.)

The acid is indeed formed when benzidine and phthalic anhydride are heated together, but the addition of nitrobenzene ensures that the materials are brought into close contact with each other.

The reaction proceeds in the same way when derivatives or substitution products of benzidine are used, or when di- or tetra-chlorophthalic anhydrides or succinic anhydrides are employed. Only the diphthalamic acids obtained from phthalic anhydride and benzidine, tolidine, and dianisidine, however, are described in this paper.

These diphthalamic acids are white powders, which are insoluble in all the ordinary solvents, but dissolve in sodium carbonate forming the corresponding sodium salts. They do not melt when heated, but lose water with the production of the corresponding diphthalimino-derivatives (compare formula I), which, in the case of tolidine and dianisidine, as well as benzidine, have been previously described.

An interesting result is obtained when the diphthalamic acids are fused with resorcinol in the presence of zinc chloride; colouring matters are obtained which correspond with that produced by condensing phthalic anhydride with resorcinol, namely, fluorescein, the constitution, for example, in the case of the diphthalamic acid derived from benzidine being represented by formula (IV):



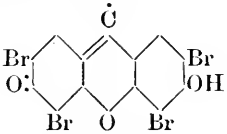
(IV.)

In the case of tolidine there was also obtained an intermediate colouring matter containing only one fluorescein nucleus.

These colouring matters possess the property of dyeing cotton without a mordant, doubtless owing to the presence of the diphenyl group, in bluish-pink shades; they have also an affinity for wool and silk, but the dyeings are not very fast.

They may also be prepared (i) by fusing a mixture of the diamine (benzidine, tolidine, dianisidine, etc.) with phthalic anhydride and resorcinol in the presence of zinc chloride, which is, perhaps, the most convenient method of preparation; (ii) by condensing fluorescein with the diamine and the hydrochloride of the diamine; and (iii) by fusing the diphthalyl derivatives of the diamines with resorcinol and zinc chloride, but the yield in this case is poor.

They appear to behave very similarly to fluorescein; thus, for instance, when brominated they yield octabromo-derivatives corresponding with eosin; that is, the bromine atoms take up the following positions in each pyronine ring:



This is proved by the fact that the same colouring matters are produced from eosin, the diamine, and the diamine hydrochloride.

The brominated colouring matters also dye cotton without a mordant, as well as wool and silk, the shades produced being yellower than those given by the dyestuffs from which they are prepared.

The colouring matters here described decompose when heated to a high temperature.

The above reaction has also been found to take place when diethyl-*m*-aminophenol is used instead of resorcinol, the corresponding substituted rhodamine-*B* being produced. Condensation of the diphthalamic acids with quinol, catechol, and pyrogallol, or condensation of these phenols with the *p*-diamine, and phthalic anhydride furnishes brown colouring matters which are probably of a different type from those mentioned above; but these extensions of what appears to be a general reaction have not yet been fully worked out.

EXPERIMENTAL.

Preparation of the Diphthalamic Acids.

The diphthalamic acids are prepared by mixing phthalic anhydride (2 mols.) with the diamine (1 mol.), moistening with nitrobenzene, and heating the mixture on a water-bath to 100° for an hour.

The calculated amount of sodium carbonate necessary to neutralise the acid is added, and the nitrobenzene removed by a current of steam. The solution is filtered if necessary, and either allowed to cool, when the sodium salt crystallises out, or acidified with hydrochloric acid, when the diphthalamic acid is precipitated as a white, flocculent mass.

Diphenyl-4:4′-diphthalamic acid, $C_{28}H_{20}O_6N_2$, is a white powder, insoluble in all the ordinary solvents, and when heated it turns yellow with the formation of diphthalylbenzidine:

0·1688 neutralised 40·2 c.c. NaOH (1 c.c. = 0·0007 gram), which is the theoretical quantity.

The *sodium* salt crystallises in leaflets:

0·2932 gave 0·764 Na_2SO_4. Na = 8·8.

$C_{28}H_{18}O_6N_2Na_2$ requires Na = 8·8 per cent.

3:3′-*Dimethyldiphenyl*-4:4′-*diphthalamic acid*, $C_{30}H_{24}O_6N_2$, prepared from tolidine, resembles the acid just described:

0·1044 neutralised 23·5 c.c. NaOH (1 c.c. = 0·0007 gram), which is the theoretical quantity.

The *sodium* salt crystallises in leaflets:

0·0862 gave 0·0224 Na_2SO_4. Na = 8·4.

$C_{30}H_{22}O_6N_2Na_2$ requires Na = 8·3 per cent.

3:3′-*Dimethoxydiphenyl*-4:4′-*diphthalamic acid*, $C_{30}H_{24}O_8N_2$, prepared from dianisidine, is similar to the above:

0·2434 neutralised 8·9 c.c. of *N*/10-NaOH, whereas theory requires 9·0 c.c.

The *sodium* salt is obtained in stellate crystals when the acid is dissolved in excess of sodium carbonate and sodium chloride added in insufficient amount to cause immediate precipitation:

0·3146 gave 0·0524 Na_2SO_4. Na = 7·8.

$C_{30}H_{22}O_8N_2Na_2$ requires Na = 7·9 per cent.

This salt is easily hydrolysed, for when it is dissolved in hot water the acid separates out.

Preparation of the Colouring Matters.

The general method of preparation of the colouring matters is to mix together the diphthalamic acid (1 mol.), resorcinol (4 mols.), and anhydrous zinc chloride, and to heat the mixture at about 200—220° for about two hours. Alternately a mixture of the diamine (1 mol.), phthalic anhydride (2 mols.), resorcinol (8 mols.), and zinc chloride is similarly heated. The fusion is powdered, extracted first with dilute hydrochloric acid to remove zinc salts, and then with sodium carbonate to remove a yellow, fluorescent colouring matter (which gives the purple colouring matter on fusion with resorcinol and zinc chloride). The residue is treated with warm aqueous sodium hydroxide, which dissolves the colouring matter, and the solution is filtered from a colourless by-product (the nature of the latter has not yet been elucidated; it dissolves on boiling for some time with sodium hydroxide solution, and when fused with resorcinol and zinc chloride it yields the colouring matter). The filtrate is either acidified to obtain the free colouring matter or treated with sodium chloride to "salt out" the sodium salt. An alternative method is to omit the above extraction with sodium carbonate and to separate the yellow by-product by careful "salting out" of the solution in sodium hydroxide when the yellow by-product remains in solution.

Bromination of the colouring matters is effected by treating the alcoholic solution with the calculated amount of bromine when the bromo-derivative separates out.

Difluoresceinbenzidide (formula IV) is a purple powder which dissolves in alkali hydroxides to a bluish-red solution and in alcohol to a purple solution. It dissolves in sulphuric acid with a green colour, and dyes wool, silk, and cotton in bluish-pink shades. For analysis it was crystallised from alcohol:

0·4946 gave 15·1 c.c. N_2 at 21° and 756·4 mm. N=3·54.

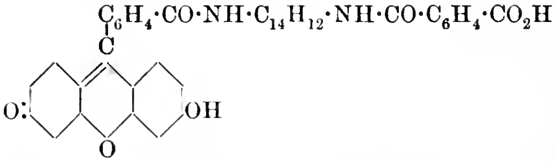
$C_{52}H_{32}O_8N_2$ requires N=3·44 per cent.

Dieosinbenzidide is a purple powder, which dyes wool, silk, and cotton in yellowish-pink shades:

0·1338 gave 0·1394 AgBr. Br=44·3.

$C_{52}H_{24}O_8N_2Br_8$ requires Br=44·3 per cent.

In preparing the colouring matter from tolidine it was found that if the fusion is conducted at about 190—195° only one of the carboxylic groups of the diphthalamic acid entered into reaction; the same took place also when tolidine was condensed with phthalic anhydride and resorcinol at this temperature. The substance obtained has therefore the formula:



,

and is *4-fluoresceinamino-3:3′-dimethyldiphenyl-4′-phthalamic acid.* This colouring matter dyes in redder shades than difluoresceinbenzidide:

0·4324 gave 15·4 c.c. N_2 at 21·5° and 769 mm. N=4·18.

$C_{42}H_{30}O_7N_2$ requires N=4·15 per cent.

On bromination it yields 4-*eosinamino*-3:3′-*dimethyldiphenyl*-4′-*phthalamic acid*, which produces yellower shades than the preceding substance:

0·6243 gave 14·5 c.c. N_2 at 12·5° and 753·4 mm. N = 2·75.

$C_{42}H_{26}O_7N_2Br_4$ requires N = 2·83 per cent.

When the fusion of tolidine, phthalic anhydride, and resorcinol (with zinc chloride) is carried out at 230—245°, both carboxylic groups react, and *difluoresceintolidide* is produced. This is a purple powder, which dyes in bluish-pink shades:

0·6837 gave 18 c.c. N_2 at 18° and 768·35 mm. N = 3·1.

$C_{54}H_{36}O_8N_2$ requires N = 3·3 per cent.

Difluoresceindianisidide, prepared from dianisidine, dyes in bluer shades than the benzidide or tolidide:

0·6323 gave 20·3 c.c. N_2 at 19° and 761 mm. N = 3·78.

$C_{54}H_{36}O_{10}N_2$ requires N = 3·21 per cent.

Dieosindianisidide, prepared by brominating the above, dyes in bluish-pink shades:

0·1085 gave 0·1070 AgBr. Br = 42·0.

$C_{54}H_{28}O_{10}N_2Br_8$ requires Br = 42·5 per cent.

The expenses of this investigation have been partly defrayed by a grant from the Research Fund of the Chemical Society, for which the authors desire to express their thanks.

CCXLIV.—*The Relation between Constitution and Rotatory Power amongst Derivatives of Tetrahydroquinaldine.*

By William Jackson Pope and Thomas Field Winmill.

A little consideration suffices to show the difficulty of conceiving how any simple relation of a quantitative character can exist between the constitution of an optically active substance and its rotation constants. When a plane-polarised light-ray enters an optically active liquid, it is resolved into two circularly and oppositely polarised rays which travel at different velocities through the liquid; the extent to which the one circularly polarised ray is retarded with respect to the other determines the sense, and measures the magnitude, of the angle which the plane of polarisation of the original entrant ray makes with that of the single emergent plane polarised ray produced when the two circularly-polarised rays leave the liquid. It is at present impossible to see how any simple quantitative relationship can exist between the nature of the optically active liquid and the difference in velocity of propagation of the two circularly-polarised rays mentioned. The difficulty suggested is enhanced by the fact that no quantitative measure of the degree of asymmetry of a molecular configuration appears at present to be available; a configuration is either asymmetric or enantiomorphous, namely, devoid of a centre of symmetry, or possesses such elements of symmetry as render it identical with its mirror image. In the general case of a solid figure or configuration possessing no elements of symmetry, it appears impossible to define the *degree* of asymmetry in any logical manner; the artificial and arbitrary definitions devised by Crum Brown, Guye, and others have been found useless except as stimulants to investigation.

Notwithstanding the above and other considerations which seem to stamp the molecular rotatory power as an extremely complex function of the chemical nature of an optically active substance, it cannot be doubted that in great numbers of cases a comparatively simple relation, roughly quantitative in character, is observable between chemical constitution and rotatory power. Frequently, as in cases studied by Frankland, Cohen, and others, the relation is between the constitution and molecular rotatory power of isomeric benzene derivatives; and in general, as is obvious from Pickard's work, a progressive change in rotation constants occurs throughout a homologous series. A convenient summary of these cases has been published recently (Frankland, Presidential Address, this vol., p. 654). In yet other cases a fairly close quantitative relation is observed between the changes in the rotation constants which attend substitution by specific radicles (Perkin and Pope, Trans., 1911, **99**, 1525).

The rule, which is very generally obeyed, that in isomeric optically active benzene derivatives, ortho-substitution causes a smaller, and para-substitution produces a greater, effect on the rotation constants than does meta-substitution, has been extended by Frankland to the rule that the molecular rotatory powers are in the order:

ortho, unsubstituted phenyl, meta, para

(Trans., 1896, **69**, 1583); the expanded rule is also generally obeyed, although not so frequently as is the original one. Inasmuch, however, as most of the available experimental data refer to optically active esters, and the differences between the molecular rotations of isomeric members of the series are frequently not very great, it seemed desirable to study a set of compounds of a different character, in which greater variations in molecular rotation might be expected to occur amongst isomeric substances. Since *l*-tetrahydroquinaldine, with $[\alpha]_D$ −61·20°, yields a benzoyl derivative with $[\alpha]_D$ +230°, it is to be anticipated that the rotation constants of the secondary base would be greatly altered by substitution; the present paper gives the rotation constants for a number of substituted benzoyl-*l*-tetrahydroquinaldines in several solvents for three wave-lengths.

Benzoyl-l-*tetrahydroquinaldine*, $C_{10}H_{12}N\cdot CO\cdot C_6H_5$.

This, and the following acidic derivatives of the base, were prepared by the Schotten-Baumann reaction from pure *l*-tetrahydroquinaldine prepared as previously described (Pope and Peachey, Trans., 1899, **75**, 1066); all the observed rotatory powers stated in the present paper were measured in 4-dcm. tubes at 20°, and those for the benzoyl derivative in ethyl alcoholic solution are quoted from Pope and Read (Trans., 1910, **97**, 2206). The mean rotatory dispersions for the several solvents are the following:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	1·215	1·215	1·222	1·222
Hg_{yellow}/Na_{yellow}	1·051	1·046	1·047	1·050

o-*Nitrobenzoyl*-l-*tetrahydroquinaldine*, $C_{10}H_{12}N\cdot CO\cdot C_6H_4\cdot NO_2$.

This compound was prepared with the aid of *o*-nitrobenzoyl chloride, and crystallises from alcohol in lemon-yellow needles melting at 110°; it dissolves readily in alcohol, acetic acid, benzene, or acetone, giving pale yellow solutions:

0·1205 gave 0·3032 CO_2 and 0·0601 H_2O. C = 68·7; H = 5·5.
$C_{17}H_{16}O_3N_2$ requires C = 68·9; H = 5·4 per cent.

The mean rotatory dispersions are as follows:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	−0·1181	+1·701	−1·213	+0·483
Hg_{yellow}/Na_{yellow}	+0·805	+1·147	+0·4995	+0·917

This substance exhibits quite abnormal rotation constants. For all three wave-lengths used it is dextrorotatory in acetic acid, and lævorotatory in benzene solution; in alcohol and acetone it is dextrorotatory for the sodium and mercury-yellow rays, and lævorotatory for mercury-green light.

m-*Nitrobenzoyl*-l-*tetrahydroquinaldine*, $C_{10}H_{12}N\cdot CO\cdot C_6H_4\cdot NO_2$.

This substance, prepared from the base and *m*-nitrobenzoyl chloride in presence of dilute sodium hydroxide, crystallises from alcohol in colourless needles melting at 97°; the corresponding externally compensated compound is described as forming pale yellow leaflets melting at 114° (Walter, *Ber.*, 1892, **25**, 1269):

0·1106 gave 0·2790 CO_2 and 0·0552 H_2O. C=68·8; H=5·5.

$C_{17}H_{16}O_3N_2$ requires C=68·9; H=5·4 per cent.

The mean rotatory dispersions are as follows:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	1·210	1·215	1·223	1·226
Hg_{yellow}/Na_{yellow}	1·048	1·053	1·051	1·054

p-*Nitrobenzoyl*-l-*tetrahydroquinaldine*, $C_{10}H_{12}N\cdot CO\cdot C_6H_4\cdot NO_2$.

This compound, prepared with the aid of *p*-nitrobenzoyl chloride, is only obtained in the solid state with difficulty; on crystallisation first from dilute alcohol and subsequently from a mixture of benzene and light petroleum, it forms large, pale yellow crystals melting at 110°. It is readily soluble in the ordinary organic solvents, yielding yellow solutions:

0·1260 gave 0·3187 CO_2 and 0·0624 H_2O. C=69·0; H=5·5.

$C_{17}H_{16}O_3N_2$ requires C=68·9; H=5·4 per cent.

The mean rotatory dispersions are as follows:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	1·244	1·237	1·247	1·248
Hg_{yellow}/Na_{yellow}	1·051	1·053	1·054	1·057

As was anticipated from the previous argument (p. 2311), the strongly lævorotatory *l*-tetrahydroquinaldine yields acidic derivatives which differ widely amongst themselves, and from the parent base, in molecular rotatory power; the great sensitiveness of the rotation constants of the optically active secondary base to substitution makes it possible to confirm some of the conclusions of previous authors in a somewhat striking manner, notwithstanding the variations suffered by the molecular rotation of each derivative with the solvent and the wave-length. A consideration of the tables of experimental data given above shows that for each solvent, and for all wave-lengths, the molecular rotatory powers of the nitrobenzoyl-*l*-tetrahydroquinaldines are in the order: ortho, meta, para; the molecular rotatory powers in benzene solution, also for all wave-lengths, are in the order prescribed by the Frankland rule, namely, ortho, phenyl, meta, para. Inasmuch as the latter rule was deduced from observations made on substances totally different in type to those above described, the evidence now adduced must be regarded as of importance. It appears justifiable to conclude that the Frankland rule, based upon somewhat crude statical conceptions (Trans., 1896, **69**, 1583), does actually hold, but that the numerical values of the molecular rotatory powers are affected, within limits, by influences not embraced by the original mechanical scheme.

It may here be noted that the variability of rotation constants with solvent was attributed by Pope and Peachey (Trans., 1899, **75**, 1111), in the main, to changes in association of the optically active substance produced by the solvent; Patterson opposed this view (Trans., 1901, **79**, 186), and strongly advocated the idea that the cause of variation of rotation constant with solvent is to be found in variation of the internal pressure prevailing in the solution. Patterson's later papers indicate that he has abandoned the view that internal pressure is an operative factor in connexion with variations in the rotatory power, whilst Walden (*Ber.*, 1905, **38**, 345) apparently adopts the view that, in the main, the association factor determines the rotatory power. The complex character of the problem under discussion discourages any attempt to draw a final judgment between the several views which have been advanced as guides to further investigation; but the arguments advanced in 1899 still hold good, and the method there applied for determining whether a given externally compensated substance is, or is not, existent as a racemic compound in the liquid state, must still be regarded as more simple and direct in its application than the viscometric method (see Dunstan and Thole, Trans., 1910, **97**, 1249).

p-*Toluoyl*-l-*tetrahydroquinaldine*, $C_{10}H_{12}N{\cdot}CO{\cdot}C_6H_4{\cdot}CH_3$.

The change in the molecular rotatory power of *l*-tetrahydroquinaldine which attends substitution by the benzoyl radicle and its *o*-, *m*-, and *p*-nitro-derivatives, has been shown to be roughly in accordance with the mechanical conception enunciated by Frankland; since the mass of the substituting group is regarded as an important factor in this view, it appeared of interest to ascertain in what way the molecular rotatory power is affected by replacing the heavy nitro-group by the lighter methyl radicle. As the accompanying tables indicate that the introduction of a nitro-group in the para-position in benzoyl-*l*-tetrahydroquinaldine produces the maximum change in rotatory power, it was to be anticipated that *p*-toluoyl-*l*-tetrahydroquinaldine should exhibit rotation constants of the same type of variability as, but of smaller magnitude than, those of *p*-nitrobenzoyl-*l*-tetrahydroquinaldine; the accompanying table of experimental data shows that this is actually the case. *p*-Nitrobenzoyl-*l*-tetrahydroquinaldine and *p*-toluoyl-*l*-tetrahydroquinaldine give rotation constants which for the several solvents used are in the order: acetic acid, alcohol, acetone, benzene; but the absolute values for the molecular constants are considerably smaller for the latter than for the former substance.

p-Toluoyl-*l*-tetrahydroquinaldine, prepared from *p*-toluoyl chloride and the secondary base, crystallises from dilute alcohol in fine, colourless needles, which melt at 113°; it is very readily soluble in the ordinary organic solvents:

0·1333 gave 0·3986 CO_2 and 0·0880 H_2O. C=81·5; H=7·2.
$C_{18}H_{19}ON$ requires C=81·5; H=7·2 per cent.

The mean rotatory dispersions are as follows:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	1·213	1·217	1·217	1·218
Hg_{yellow}/Na_{yellow}	1·04	1·053	1·049	1·047

Toluene-p-*sulphonyl*-l-*tetrahydroquinaldine*, $C_{10}H_{12}N\cdot SO_2\cdot C_6H_4\cdot CH_3$.

In a recent paper (Pope and Gibson, this vol., p. 1702) it has been shown that, whilst the benzoylation of *d-sec.*-butylamine yields a benzoyl derivative of considerable molecular rotatory power and marked rotatory dispersion, benzenesulphonyl-*d-sec.*-butylamine is but slightly optically active, and exhibits practically the same specific rotation for the several wave-lengths used; toluene-*p*-sulphonyl-*d-sec.*-butylamine is similarly but slightly optically active, and shows no rotatory dispersion. The sulpho-acidic derivatives of the optically active *sec.*-butylamines thus exhibit rotation constants which are abnormal in comparison with those of the carboxy-acidic derivatives of the base. In connexion with the quantitative meaning of rotation constants now under discussion, it was thus of interest to ascertain whether the abnormality is peculiar to derivatives of *d-sec.*-butylamine or whether abnormalities are to be observed amongst the sulpho-acidic derivatives of *l*-tetrahydroquinaldine. For this reason toluene-*p*-sulphonyl-*l*-tetrahydroquinaldine was prepared and examined.

The latter substance, prepared by the Schotten-Baumann reaction, dissolves readily in the ordinary organic solvents, and crystallises from alcohol in large, colourless pyramids on a square base, which melt at 109°:

0·1036 gave 0·2575 CO_2 and 0·0593 H_2O. C=67·8; H=6·4.
$C_{17}H_{19}O_2NS$ requires C=67·8; H=6·3 per cent.

The mean rotatory dispersions are as follows:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	1·195	1·213	1·203	1·190
Hg_{yellow}/Na_{yellow}	1·045	1·056	1·048	1·042

The accompanying table, stating the rotatory powers of this substance, shows that the latter exhibits an altogether anomalous optical behaviour; whilst *p*-toluoyl-*l*-tetrahydroquinaldine is a strongly dextrorotatory compound, the corresponding toluene-*p*-sulphonyl derivative is strongly lævorotatory in the several solvents used. At the same time the rotatory dispersions for the two substances are of the same order of magnitude. It will be noted that a curious confirmation is thus supplied of the applicability of the static view advanced by Frankland concerning the main factor which determines molecular rotatory power; the heavy group, SO_2, placed close to the optically active nucleus in *l*-tetrahydroquinaldine, preserves the lævorotation of the parent base which the lighter group, CO, is not able to maintain.

Nitrobenzene-m-*sulphonyl*-l-*tetrahydroquinaldine*, $C_{10}H_{12}N \cdot SO_2 \cdot C_6H_4 \cdot NO_2$.

The replacement of the group CO in *p*-toluoyl-*l*-tetrahydroquinaldine by the heavier group SO_2, acting close to the optically active nucleus, has been found above to convert a strongly dextrorotatory substance into a strongly lævorotatory one; if the static view concerning the determining factor in the magnitude of molecular rotatory power is applicable, it would be expected that on replacing the group CO by the radicle SO_2 in a derivative of lower rotatory power, the latter value should be influenced to a smaller extent than in the foregoing case. For this reason nitrobenzene-*m*-sulphonyl-*l*-tetrahydroquinaldine was prepared and examined.

Nitrobenzene-*m*-sulphonyl chloride condenses readily with the optically active base under the usual conditions; the product separates from alcoholic solution in colourless crystals melting at 132°, and is sparingly soluble in alcohol, the saturated solution containing 1·5 per cent. of the substance at 20°:

0·1122 gave 0·2379 CO_2 and 0·0500 H_2O. C=57·8; H=4·9.

$C_{16}H_{16}O_4N_2S$ requires C=57·8; H=4·8 per cent.

The mean rotatory dispersions have the following values:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	1·207	1·197	1·230	1·207
Hg_{yellow}/Na_{yellow}	1·076	1·049	1·065	1·052

The accompanying table of the rotation constants indicates that, as suggested above, the replacement of the group CO in the dextrorotatory *m*-nitrobenzoyl-*l*-tetrahydroquinaldine by the group SO_2, leads to the formation of a lævorotatory substance exhibiting rotation constants which, in general, are rather smaller than those of toluene-*p*-sulphonyl-*l*-tetrahydroquinaldine. Although the values of [M] for nitrobenzene-*m*-sulphonyl-*l*-tetrahydroquinaldine are considerably smaller than those for toluene-*p*-sulphonyl-*l*-tetrahydroquinaldine in alcohol, acetone, or acetic acid solution, they are slightly but distinctly larger in benzene solution.

2-*Nitrotoluene*-4-*sulphonyl*-l-*tetrahydroquinaldine*, $C_{10}H_{12}N{\cdot}SO_2{\cdot}C_6H_3Me{\cdot}NO_2$.

The condensation product of 2-nitrotoluene-4-sulphonyl chloride and *l*-tetrahydroquinaldine separates from boiling alcoholic solution in yellow crystals, which melt at 125°; it is very sparingly soluble in cold alcohol:

0·1178 gave 0·2535 CO_2 and 0·0563 H_2O. C=58·7; H=5·3.

$C_{17}H_{18}O_4N_2S$ requires C=58·9; H=5·2 per cent.

The mean rotatory dispersions are as follows:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	1·107	0·895	1·144	1·110
Hg_{yellow}/Na_{yellow}	1·023	0·967	1·025	1·033

From analogy to the behaviour of the foregoing substances it might be expected that, on introducing a methyl group para to the sulphonyl radicle in nitrobenzene-*m*-sulphonyl-*l*-tetrahydroquinaldine, the lævorotatory power of the latter substance would be lessened. It is accordingly found that whilst nitrobenzene-*m*-sulphonyl-*l*-tetrahydroquinaldine is a strongly lævorotatory compound, its para-methyl derivative is but feebly lævorotatory. The considerable variation of rotatory dispersion of the latter substance with the solvent used is noteworthy.

α-*Naphthoyl*-l-*tetrahydroquinaldine*, $C_{10}H_{12}N{\cdot}CO{\cdot}C_{10}H_7$.

α-Naphthoyl chloride was described by v. Hofmann (*Proc. Roy. Soc.*, 1868, **16**, 304) as an oil which solidifies at a low temperature, and is instantaneously hydrolysed by water; by treating α-naphthoic acid with phosphorus pentachloride we obtained the chloride as a colourless, crystalline substance, which melts at 20°, and is very slowly acted on by water. The composition of our product was checked by analysis.

α-*Naphthoyl*-l-*tetrahydroquinaldine*, prepared in the usual manner, crystallises from dilute alcohol in fine needles melting at 150°:

0·1256 gave 0·3843 CO_2 and 0·0710 H_2O. C=83·6; H=6·3.

$C_{21}H_{19}ON$ requires C=83·8; H=6·3 per cent.

The rotatory dispersions have the following mean values:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	1·238	1·247	1·239	1·238
Hg_{yellow}/Na_{yellow}	1·051	1·048	1·055	1·058

β-Naphthoyl-1-tetrahydroquinaldine, $C_{10}H_{12}N\cdot CO\cdot C_{10}H_7$.

This compound, prepared by the Schotten-Baumann reaction, crystallises from a mixture of benzene and alcohol in fine, colourless needles melting at 186°; it is readily soluble in benzene or acetic acid, sparingly so in alcohol or acetone:

0·1126 gave 0·3470 CO_2 and 0·0647 H_2O. C = 84·0; H = 6·4.
$C_{21}H_{19}ON$ requires C = 83·8; H = 6·3 per cent.

The following mean values of the rotatory dispersions were obtained:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	1·224	1·217	1·226	1·224
Hg_{yellow}/Na_{yellow}	1·059	1·050	1·051	1·053

The argument stated above, by means of which the molecular rotation constants are connected with the constitution of the tetrahydroquinaldine derivative, is not readily applied to the naphthoyltetrahydroquinaldines; it will be seen from the accompanying tables of rotatory constants that both derivatives are strongly dextrorotatory, and that the molecular rotatory powers of the β-isomeride vary much more than do those of the α-compound with change of solvent.

Naphthalene-α-sulphonyl-1-tetrahydroquinaldine, $C_{10}H_{12}N\cdot SO_2\cdot C_{10}H_7$.

This substance is readily prepared in the usual manner, and crystallises from boiling alcohol, in which it is very sparingly soluble, in colourless needles melting at 129°; it dissolves easily in acetone to give a practically colourless solution, which rapidly becomes bright yellow, but without at the same time showing mutarotation:

0·1123 gave 0·2933 CO_2 and 0·0582 H_2O. C = 71·2; H = 5·8.
$C_{20}H_{19}O_2NS$ requires C = 71·2; H = 5·7 per cent.

The mean rotatory dispersions are as follows:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	1·299	1·314	1·260	1·287
Hg_{yellow}/Na_{yellow}	1·069	1·078	1·042	1·070

Naphthalene-β-sulphonyl-1-tetrahydroquinaldine, $C_{10}H_{12}N\cdot SO_2\cdot C_{10}H_7$.

This compound is readily soluble in most organic solvents, and crystallises from alcohol in colourless leaflets melting at 89°:

0·1497 gave 0·3922 CO_2 and 0·0764 H_2O. C = 71·4; H = 5·7.
$C_{20}H_{19}O_2NS$ requires C = 71·2; H = 5·7 per cent.

Benzoyl-1-tetrahydroquinaldine.

Solvent.	Grams per 100 c.c.	α.			[α].			[M].		
		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
Ethyl alcohol ...	0·5837	+9·40	+8·08	+7·70	+402·6	+346·1	+329·8	+1010	+869	+828
,, ...	1·6890	26·84	23·12	22·07	397·3	342·2	326·7	997	859	820
Benzene	0·3441	4·13	3·56	3·40	300·0	258·6	247·0	753	649	620
,, ...	0·6624	7·96	6·84	6·55	300·4	258·2	247·2	754	648	620·5
,, ...	1·3396	16·07	13·84	13·22	299·9	258·3	246·7	753	648·4	619·3
Acetone...........	0·3248	5·06	4·33	4·14	389·5	333·3	318·7	977·6	836·6	799·9
,, ...	0·6595	10·26	8·80	8·40	388·9	333·5	318·4	976·1	837·1	799·2
,, ...	1·3265	20·64	17·69	16·88	389·0	333·3	318·1	976·4	836·6	798·5
Acetic acid	0·3375	6·01	5·165	4·92	445·3	382·7	364·5	1117·7	960·6	914·9
,, ...	0·6797	12·12	10·42	9·91	445·8	383·2	364·5	1118·9	961·8	914·9
,, ...	1·3309	23·70	20·38	19·40	445·2	382·8	364·5	1117·5	960·8	914·9

o-Nitrobenzoyl-1-tetrahydroquinaldine.

Solvent.	Grams per 100 c.c.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
Ethyl alcohol ...	0·8200	−0·065	+0·46	+0·56	−1·98	+14·0	+17·07	−5·79	+40·9	+49·9
,, ...	1·2390	−0·10	+0·69	+0·85	−2·02	+13·9	+17·15	−5·89	+40·7	+50·0
,, ...	1·8332	−0·15	+0·98	+1·255	−2·05	+13·4	+17·11	−5·97	+39·0	+50·0
Benzene	0·6652	−2·65	−1·78	−1·55	−99·6	−66·9	−58·3	−290·8	−195·3	−170·1
,, ...	1·2307	−4·89	−3·31	−2·87	−99·3	−67·2	−58·3	−290·1	−196·3	−170·2
,, ...	1·7644	−6·99	−4·71	−4·13	−99·0	−66·8	−58·5	−289·3	−194·9	−170·8
Acetone...........	0·6717	−0·31	+0·135	+0·26	−11·5	+5·0	+9·68	−34·1	+14·6	+28·3
,, ...	1·1566	−0·52	+0·23	+0·45	−11·3	+5·0	+9·73	−33·5	+14·5	+28·4
,, ...	2·1108	−1·05	+0·38	+0·81	−12·4	+4·5	+9·60	−36·3	+13·2	+28·0
Acetic acid	0·6906	+0·40	+0·76	+0·83	+14·5	+27·5	+30·0	+42·3	+80·4	+87·7
,, ...	1·8484	+1·07	+2·03	+2·22	+14·5	+27·5	+30·0	+42·3	+80·4	+87·7

m-*Nitrobenzoyl*-l-*tetrahydroquinaldine.*

Alcohol	0·7053	+8·25	+7·15	+6·81	+292·5	+253·4	+241·4	+865·6	+750·2	+714·5
,, ...	1·1043	12·94	11·20	10·68	292·0	253·5	241·7	867·0	750·4	715·5
,, ...	1·7303	20·25	17·49	16·72	292·6	252·8	241·6	865·6	748·0	715·1
Benzene	0·7753	8·63	7·49	7·10	278·3	241·5	229·0	823·7	714·8	677·8
,, ...	1·0513	11·70	10·13	9·64	278·9	241·5	229·7	825·4	714·8	680·0
,, ...	1·6752	18·68	16·18	15·38	278·8	241·5	229·6	825·2	714·8	679·4
Acetone...........	0·6843	8·42	7·25	6·89	307·6	264·9	251·7	910·6	784·0	745·1
,, ...	1·0710	13·17	11·32	10·76	307·4	264·3	251·2	910·0	782·2	743·2
,, ...	1·7930	21·98	18·85	17·98	306·5	262·9	250·7	907·3	780·0	742·1
Acetic acid	0·6867	8·45	7·27	6·90	307·6	264·6	250·8	910·5	783·3	742·4
,, ...	1·2717	15·59	13·40	12·72	306·5	263·5	250·1	907·2	780·0	740·4
,, ...	1·7456	21·40	18·39	17·47	306·5	263·4	250·2	907·2	779·9	740·5

p-*Nitrobenzoyl*-l-*tetrahydroquinaldine.*

Alcohol	0 3425	+6·30	+5·32	+5·06	+459·9	+388·4	+369·4	+1361·4	+1149·6	+1093·4
,, ...	0·6644	12·22	10·33	9·82	459·9	388·7	369·5	1361·1	1150·6	1093·8
,, ...	1·3376	24·57	20·77	19·79	459·2	388·2	369·9	1359·3	1149·1	1094·9
Benzene...........	0·3384	5·37	4·57	4·34	396·7	337·6	320·7	1174·1	999·2	949·1
,, ...	0·6564	10·40	8·87	8·41	396·1	337·9	320·3	1172·5	1000·0	948·2
,, ...	1·3317	21·12	18·00	17·08	396·5	337·9	320·7	1173·7	1000·3	949·2
Acetone...........	0·3288	5·78	4·89	4·64	439·5	371·8	352·8	1301·0	1100·7	1044·4
,, ...	0·6717	11·82	9·99	9·47	439·6	371·8	352·5	1301·1	1100·6	1044·8
,, ...	1·3317	23·44	19·80	18·80	440·1	371·7	353·0	1302·7	1100·4	1044·8
Acetic acid	0·3528	6·68	5·66	5·36	473·4	401·1	379·1	1401·1	1187·2	1122·1
,, ...	0·6670	12·64	10·71	10·14	473·7	401·4	380·0	1402·3	1188·2	1124·9
,, ...	1·3402	25·41	21·54	20·35	473·9	401·8	379·6	1403·0	1189·2	1123·6

p-*Toluoyl*-1-*tetrahydroquinaldine.*

		α.			[α].			[M].		
Solvent.	Grams per 100 c.c.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
Alcohol	0·3515	+5·69	+4·88	+4·70	+404·7	+347·1	+334·3	+1073·5	+919·9	+885·5
,, ...	0·6780	10·85	9·31	8·94	404·8	347·4	333·6	1073·8	920·7	884·0
,, ...	1·3369	21·63	18·57	17·82	404·5	347·2	333·2	1073·0	920·2	883·1
Benzene............	0·3338	4·08	3·535	3·35	305·6	264·8	250·9	809·8	701·7	665·0
,, ...	0·6797	8·31	7·20	6·84	305·6	264·8	251·5	809·9	701·7	666·7
,, ...	1·3333	16·29	14·10	13·41	305·5	264·4	251·5	809·5	700·9	666·4
Acetone............	0·3404	5·36	4·62	4·41	393·6	339·3	323·8	1045·0	899·0	858·2
,, ...	0·6702	10·57	9·10	8·66	394·2	339·4	323·0	1044·8	899·5	855·9
,, ...	1·3426	21·14	18·20	17·38	393·7	338·9	323·6	1043·2	898·1	857·6
Acetic acid	0·3231	5·84	5·02	4·80	451·9	388·5	371·4	1197·5	1029·4	984·2
,, ...	0·6597	11·93	10·25	9·80	452·1	388·5	371·4	1198·1	1029·4	984·2
,, ...	1·3472	24·36	20·94	19·98	452·0	388·6	370·7	1197·9	1029·7	982·5

Toluene-p-*sulphonyl*-1-*tetrahydroquinaldine.*

		α.			[α].			[M].		
Solvent.	Grams per 100 c.c.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.	Hg_{green}.	$\text{Hg}_{\text{yellow}}$.	$\text{Na}_{\text{yellow}}$.
Alcohol	0·3392	−2·22	−1·94	−1·845	−163·7	−143·0	−136·0	−492·7	−430·4	−409·4
,, ...	0·6687	4·38	3·83	3·66	163·7	143·2	136·8	492·7	431·0	411·8
,, ...	1·3207	8·66	7·56	7·25	163·9	143·1	137·2	493·3	430·7	413·0
Benzene............	0·3254	2·12	1·845	1·75	162·9	141·7	134·4	490·3	426·5	404·5
,, ...	0·6447	4·20	3·65	3·46	162·9	141·5	134·2	490·3	425·9	403·9
,, ...	1·3029	8·47	7·39	6·99	162·7	141·9	134·2	489·7	427·1	403·9
Acetone............	0·3259	2·02	1·76	1·68	154·9	135·0	128·9	466·2	406·3	388·0
,, ...	0·6637	4·11	3·58	3·42	154·8	134·9	128·8	465·9	406·0	387·7
,, ...	1·3349	8·28	7·22	6·88	155·1	135·2	128·8	466·9	406·9	387·7
Acetic acid	0·3478	2·03	1·77	1·70	145·9	127·2	122·2	429·1	382·9	367·8
,, ...	0·6560	3·84	3·33	3·20	146·3	126·9	121·9	440·3	382·0	366·9
,, ...	1·3179	7·69	6·70	6·43	145·9	127·1	122·0	439·1	382·6	367·3

Nitrobenzene-m-*sulphonyl*-l-*tetrahydroquinaldine.*

Alcohol…………	0·3692	−1·52	−1·36	−1·265	−102·9	−92·0	−85·6	−341·7	−305·6	−284·3
,, …………	0·7770	3·21	2·85	2·71	103·3	91·7	85·2	342·9	304·5	282·9
Benzene…………	0·3365	2·00	1·75	1·67	148·5	130·0	124·0	493·2	431·6	411·9
,, …………	0·7467	4·43	3·88	3·69	148·3	129·9	123·6	492·4	431·3	410·3
,, …………	1·4096	8·36	7·33	7·00	148·3	130·0	124·2	492·3	431·6	412·1
Acetone ………	0·3802	1·88	1·63	1·53	123·7	107·2	100·6	410·4	355·8	334·0
,, ………	0·7595	3·76	3·26	3·06	124·0	107·3	100·7	411·8	356·2	334·4
,, ………	1·1664	5·78	5·00	4·70	123·9	107·2	100·7	411·3	355·8	334·3
Acetic acid ……	0·3857	1·805	1·575	1·495	117·0	102·0	96·9	388·4	338·9	321·7
,, ……	0·6739	3·15	2·74	2·60	116·9	101·7	96·5	388·0	337·5	320·4
,, ……	1·5098	7·04	6·14	5·84	116·9	101·9	96·9	387·9	338·3	321·8

2-*Nitrotoluene*-4-*sulphonyl*-l-*tetrahydroquinaldine.*

Alcohol ……	0·3438	−0·74	−0·685	−0·67	−53·8	−49·8	−48·7	−186·2	−172·3	−168·6
,, ……	0·6781	1·465	1·35	1·32	54·0	49·8	48·7	186·9	172·2	168·4
Benzene…………	0·3278	0·245	0·265	0·275	18·7	20·2	21·0	64·7	69·9	72·6
,, …………	0·6744	0·51	0·55	0·565	18·9	20·4	20·9	65·4	70·5	72·5
,, …………	1·3212	1·00	1·08	1·12	18·9	20·4	21·2	65·5	70·7	73·3
Acetone…………	0·3796	0·92	0·825	0·805	60·6	54·3	53·0	209·6	188·0	183·4
,, …………	0·6665	1·62	1·45	1·415	60·8	54·4	53·1	210·2	188·2	183·6
,, …………	1·2585	3·06	2·74	2·675	60·8	54·4	53·1	210·3	188·3	183·9
Acetic acid ……	0·3481	0·42	0·39	0·38	30·2	28·0	27·3	104·4	96·9	94·4
,, ……	0·6770	0·82	0·76	0·735	30·3	28·1	27·1	104·8	97·1	93·9
,, ……	1·2909	1·55	1·45	1·40	30·0	28·1	27·1	103·9	97·2	93·8

a-Naphthoyl-1-tetrahydroquinaldine.

Solvent.	Grams per 100 c.c.	α.			[α].			[M].		
		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
Alcohol	0·3337	+6·55	+5·56	+5·29	+490·6	+416·4	+396·2	+1476·7	+1253·4	+1192·6
,, ...	0·6750	13·25	11·26	10·70	490·8	417·0	396·3	1477·3	1255·2	1192·9
,, ...	1·3336	26·14	22·25	21·12	490·0	416·2	359·9	1474·9	1262·8	1191·7
Benzene...........	0·3421	5·78	4·85	4·63	422·4	354·4	338·3	1271·4	1066·7	1018·3
,, ...	0·6647	11·22	9·46	9·00	422·0	354·6	338·5	1270·2	1067·3	1018·9
,, ...	1·3192	22·25	18·76	17·86	421·7	354·9	338·5	1269·3	1068·2	1018·9
Acetone...........	0·3341	6·38	5·44	5·15	477·4	407·1	385·4	1437·0	1221·3	1160·1
,, ...	0·6604	12·63	10·75	10·19	478·1	407·0	385·8	1439·1	1221·0	1161·3
,, ...	1·3479	25·77	21·92	20·80	478·0	406·6	385·8	1438·8	1219·8	1161·3
Acetic acid	0·3388	6·57	5·70	5·39	492·2	420·6	397·8	1481·5	1266·0	1197·4
,, ...	0·6794	13·37	11·43	10·80	492·0	420·6	397·4	1480·9	1266·0	1196·2
,, ...	1·3342	26·25	22·43	21·19	491·9	420·3	397·2	1480·6	1265·1	1195·6

β-Naphthoyl-1-tetrahydroquinaldine.

Solvent.	Grams per 100 c.c.	α.			[α].			[M].		
		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
Alcohol	0·3562	+5·92	+5·11	+4·835	+415·5	+359·5	+339·3	+1250·6	+1082·1	+1021·2
Benzene...........	0·7343	9·155	7·90	7·525	311·7	268·0	256·2	938·2	809·4	771·2
,, ...	1·2810	15·99	13·77	13·12	312·0	268·7	256·1	939·1	808·8	770·9
,, ...	2·0434	25·46	21·97	20·93	311·5	268·8	256·1	937·6	809·1	770·9
Acetone...........	0·3376	5·47	4·69	4·46	405·1	347·3	330·3	1219·3	1045·4	994·2
Acetic acid	0·6959	12·73	10·96	10·40	457·3	393·7	373·6	1376·5	1185·0	1124·5
,, ...	1·4456	26·50	22·81	21·67	457·2	393·6	373·9	1376·2	1184·7	1125·4
,, ...	2·0334	37·19	32·03	30·42	457·2	393·8	374·0	1376·2	1185·3	1225·7

Naphthalene-α-sulphonyl-1-tetrahydroquinaldine.

Alcohol	0·4065	+2·195	+1·805	+1·69	+135·0	+110·0	+103·9	+454·9	+374·1	+350·2
,, ...	0·7949	4·29	3·53	3·30	134·9	110·0	103·8	454·7	374·1	349·7
Benzene...........	0·3338	1·31	1·075	1·00	98·1	80·5	74·9	330·7	271·4	252·4
,, ...	0·6954	2·73	2·24	2·08	98·2	80·5	74·8	330·7	271·4	252·0
,, ...	1·3465	5·30	4·35	4·04	98·4	80·7	75·0	331·6	272·2	252·8
Acetone...........	0·3712	1·70	1·405	1·35	114·5	94·6	90·9	385·9	318·9	306·4
,, ...	0·7051	3·23	2·665	2·56	114·5	94·5	90·8	385·9	318·4	305·9
,, ...	1·6371	7·50	6·20	5·95	114·5	94·7	90·9	385·9	319·1	306·2
Acetic acid	0·3511	1·61	1·34	1·25	114·6	95·4	89·0	386·3	321·5	300·0
,, ...	0·6731	3·08	2·665	2·56	114·4	95·1	89·1	385·5	320·4	300·4
,, ...	1·3596	6·24	5·17	4·84	114·7	95·1	89·0	386·7	320·4	300·0

Naphthalene-β-sulphonyl-1-tetrahydroquinaldine.

Alcohol...........	0·3809	−4·22	−3·62	−3·44	−276·9	−237·6	−225·8	−933·3	−800·6	−760·8
,, ...	0·6714	7·42	6·38	6·08	276·3	237·6	226·4	931·2	800·6	763·0
,, ...	1·2570	13·88	11·93	11·31	276·1	237·3	225·0	931·0	799·6	758·1
Benzene	0·3438	3·895	3·335	3·19	283·2	242·5	232·0	954·5	817·3	781·8
,, ...	0·6791	7·70	6·605	6·31	283·5	243·2	232·3	955·3	819·5	782·9
,, ...	1·3303	15·125	12·935	12·33	284·3	243·1	231·7	957·9	819·3	781·0
Acetone	0·3404	3·60	3·09	2·95	264·4	226·9	216·6	890·9	764·7	730·1
,, ...	0·6638	7·02	6·03	5·76	264·4	227·1	216·9	890·0	765·4	731·1
Acetic acid	0·3368	3·41	2·91	2·78	253·1	216·0	206·4	853·1	728·0	695·5
,, ...	0·6537	6·60	5·65	5·40	252·4	216·1	206·5	850·7	728·2	696·0
,, ...	1·3522	13·66	11·71	11·17	252·5	216·5	206·5	851·1	729·5	697·5

The following values were obtained for the mean rotatory dispersions:

	Alcohol.	Benzene.	Acetone.	Acetic acid.
Hg_{green}/Na_{yellow}	1·224	1·223	1·220	1·223
Hg_{yellow}/Na_{yellow}	1·052	1·047	1·047	1·047

The introduction of the group SO_2 in place of the group CO in the naphthoyltetrahydroquinaldines, as in all the cases described above, greatly reduces the dextrorotation; the dextrorotatory powers observed with the naphthalene-α-sulphonyl derivative are much smaller than those of the naphthoyl compounds, and the naphthalene-β-sulphonyl derivative is strongly lævorotatory. The rotatory dispersions of the latter substance are practically independent of the solvent.

In the discussion of the above-recorded determinations of rotation constants it has proved convenient to consider whether the molecular rotatory powers of a given compound increase or diminish as a result of specific substitutions; this mode of considering the experimental results is suggested as a correct one by the Frankland rule. A curious confirmation of its correctness is furnished by an inspection of the order of change of the rotation constants of the *l*-tetrahydroquinaldine derivatives with solvent; the appended table states the order in which the four solvents used in the above determinations affect the molecular rotatory powers of the various compounds now studied; the first solvent named in each case is that in which the substance exhibits the highest rotatory power, and the last, that in which the lowest values of the rotation constants are obtained, the two other solvents being placed in their appropriate intermediate positions. In determining the order which the several solvents take in the table, the algebraic values, not the arithmetic ones, of the molecular rotation constants are alone considered; the solvent in which a high positive rotation is observed thus stands before the one in which a lower positive rotation is observed, and the solvent in which a low negative rotatory power occurs stands before that in which a large lævo-

Derivatives of	Values of [M].			
$C_{10}H_{12}N$-	Greatest.	Less.	Still less.	Least.
$C_6H_5{\cdot}CO$-	Acetic acid	Alcohol	Acetone	Benzene
o-$NO_2{\cdot}C_6H_4{\cdot}CO$-	,,	,,	,,	,,
m-$NO_2{\cdot}C_6H_4{\cdot}CO$-	Acetone	Acetic acid	Alcohol	,,
p-$NO_2{\cdot}C_6H_4{\cdot}CO$-	Acetic acid	Alcohol	Acetone	,,
p-$CH_3{\cdot}C_6H_4{\cdot}CO$-	,,	,,	,,	,,
p-$CH_3{\cdot}C_6H_4{\cdot}SO_2$-	,,	Aetone	Alcohol	,,
m-$NO_2{\cdot}C_6H_4{\cdot}SO_2$-	Alcohol	Acetic acid	,,	,,
1-CH_3-2-NO_2-4-$C_6H_3{\cdot}SO_2$-	Benzene	,,	,,	Acetone
α-$C_{10}H_7{\cdot}CO$-	Acetic acid	Alcohol	Acetone	Benzene
β-$C_{10}H_7{\cdot}CO$-	,,	,,	,,	,,
α-$C_{10}H_7{\cdot}SO_2$-	Alcohol	Acetone	Acetic acid	,,
β-$C_{10}H_7{\cdot}SO_2$-	Acetic acid	,,	Alcohol	,,

rotation is observed. In the table drawn up in this way it will be noted that in the cases of all the substances now studied, whether dextro- or lævo-rotatory, the solutions in benzene give the smallest positive values for the rotation constants, with one exception, that of the solutions of 2-nitrotoluene-4-sulphonyl-*l*-tetrahydroquinaldine, in which the highest positive values of the rotation constants are observed in benzene solutions. The fact that, in all cases but one, the benzene solutions exhibit the lowest rotatory powers seems to strongly support the legitimacy of the mode of regarding all the molecular rotation constants observed as diminished (increased) by substitution with respect to some parent substance of high positive (negative) molecular rotation; this appears to be in accordance with the static method of regarding the subject used by Frankland. It should be remarked that the solutions of most of the nitro-derivatives now described rapidly become more yellow in colour than when they are first made up; no evidence of mutarotation could, however, be obtained.

The present paper records a considerable number of exact experimental data concerning the rotation constants in various solvents of derivatives of *l*-tetrahydroquinaldine; in default of any comprehensive mode of treating such data in accordance with the sound theoretical principles, it has been found convenient to discuss them in the light of the provisional hypothesis put forward by Frankland. Although a roughly quantitative correspondence has been traced between the experimental data and the anticipations suggested by this simple mechanical scheme, it must be understood that we, and doubtless also the author of the mechanical hypothesis, regard this mode of treatment as merely provisional, and await the enunciation of some more rational theory than has hitherto been put forward concerning the relation between rotation constants, condition or state of solution, and chemical constitution.

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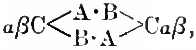
CCXLV.—*The Absence of Optical Activity in the α- and β-2 : 5-Dimethylpiperazines.*

By WILLIAM JACKSON POPE and JOHN READ.

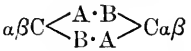
A PARTICULARLY interesting type of stereoisomerism should be illustrated by compounds of the general constitution,



$$\alpha\beta C{<}\begin{matrix}A\cdot B\\ B\cdot A\end{matrix}{>}C\alpha\beta,$$

a group of substances of which large numbers of representatives are well known; this group includes the 2:5-dialkylpiperazines, the 1:4-diketo-2:5-dialkylpiperazines (including the anhydrides of the α-aminocarboxylic acids), the 2:5-dialkyl*cyclo*hexane-1:4-diones, and many other classes of compounds which have been closely studied. Substances of the above type should exist in *cis*- and *trans*-modifications, and a consideration of the spacial arrangements of the atoms composing such molecular complexes, deduced in accordance with the van't Hoff—LeBel conception concerning the environment of a methane carbon atom, indicates that the configuration of the *cis*-compounds possesses no centre of symmetry, whilst that of the *trans*-isomerides does possess a centre of symmetry. The *cis*-compounds of the above type should thus exist in two enantiomorphously related, optically active forms, whilst the *trans*-isomerides should be internally compensated, and hence incapable of exhibiting optical activity.

In the discussion of this subject it is convenient to apply the rigidly geometrical criterion of enantiomorphism of configuration enunciated in the following definition: Every molecular configuration is enantiomorphous, and presumably capable of exhibiting optical activity, which contains no centre of symmetry; and, conversely, every molecular configuration is potentially optically inactive which contains a centre of symmetry. By the use of this definition we avoid the necessity of entering into such a discussion as that held between Ladenburg and Groth (*Ber.*, 1895, **28**, 1996), in which the erroneous, but still prevalent, view is negatived that the presence or absence of a plane of symmetry in a molecular configuration determines the non-exhibition or exhibition of optical activity by the substance; no substance of the type



$$\alpha\beta C\Big<\begin{matrix}A\cdot B\\ B\cdot A\end{matrix}\Big>C\alpha\beta$$

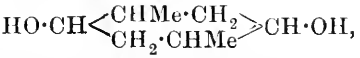
should, in accordance with the view of van't Hoff and LeBel, possess a molecular configuration exhibiting an ordinary plane of symmetry. By the use of the above definition we obviate the necessity of discussing the asymmetry of particular carbon atoms; whilst the conception of the asymmetric carbon atom proved invaluable in the hands of its originator, van't Hoff, during the early development of stereochemistry, adherence to this artificial criterion of enantiomorphism in the present more advanced stage of stereochemical investigation necessitates the construction of lengthy chains of simple geometrical arguments (compare Everest, Proc., 1911, **27**, 285), and constitutes a hindrance to progress. The fact that in an enantiomorphous molecular configuration every atom present is asymmetric, namely, devoid of geometrical association with a centre of symmetry, has been previously stated (Perkin and Pope, Trans., 1911, **99**, 1510), although the statement appears not to have been sufficiently clearly made (see Chattaway and Smiles, *Annual Reports*, 1911, **8**, 73).

A very large number of substances of the general type of constitution, $\alpha\beta C<\begin{matrix}A\cdot B\\B\cdot A\end{matrix}>C\alpha\beta$, have been obtained in two isomeric forms, corresponding presumably with the *cis*- and *trans*-molecular configurations; but in none but the one case next discussed has the *cis*-form been obtained in its two optically active modifications. Amongst the mass of data available, only one piece of stereochemical investigation, based on correct geometrical theoretical principles, has resulted in the acquisition of experimental information sufficient to illustrate fully the stereoisomerism of *cis*- and *trans*-isomerides of the type of constitution above described. Emil Fischer prepared *d*-alanyl anhydride, the *cis*-1:4-diketo-2:5-dimethylpiperazine,

$$\begin{matrix}CH_3\\H\end{matrix}>C<\begin{matrix}NH\cdot CO\\CO\cdot NH\end{matrix}>C<\begin{matrix}CH_3\\H\end{matrix}$$

(*Ber.*, 1906, **39**, 467), determined its rotation constants, and recognised that it should form an externally compensated compound with the enantiomorphously related *l*-isomeride. Later, Fischer and Raske (*Ber.*, 1906, **40**, 3981) converted the two optically active and enantiomorphously related compounds, *l*-alanyl-*d*-alanine and *d*-alanyl-*l*-alanine, into the same internally compensated and optically inactive *trans*-anhydride by dehydration. The case presented by these stereoisomerides differs from all others yet discovered in that the configuration of the *trans*- or internally compensated isomeride possesses no element of symmetry other than a centre of symmetry, whilst the configurations of the *cis*- or optically active isomerides exhibit no centre of symmetry, but possess a two-fold axis of symmetry.

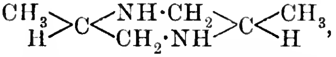
In view of the unique relationships exhibited by the type of stereochemical isomerides now under discussion, and since no other than the above well-authenticated illustration of it, worked out by Fischer, has been yet sufficiently studied, it appeared desirable to investigate other cases of the same type in order to ascertain to what extent agreement exists between the observed facts and the prognostications of stereochemical theory. A further incentive to work in this direction is found in the fact that the type of isomerism now referred to should be capable of giving rise to stereoisomerism of a somewhat complex character; thus, the 2:5-dimethyl-1:4-quinitol,



$$HO\cdot CH<\begin{matrix}CHMe\cdot CH_2\\CH_2\cdot CHMe\end{matrix}>CH\cdot OH,$$

described by Baeyer (*Ber.*, 1892, **25**, 2122) should exist in four externally compensated modifications and two internally compensated isomerides. The configurations of the eight optically active modifications possess no centres of symmetry; those of four exhibit two-fold axes of symmetry, and those of the other four do not possess these, or any other, elements of symmetry. The configurations of the two internally compensated isomerides possess centres of symmetry, but no other elements of symmetry. These several isomerides have, of course, not yet been isolated.

The most readily obtainable pair of substances which, according to the constitutions generally assigned, should exhibit the same type of configurational symmetry as do the externally and the internally compensated alanyl anhydrides, are the α- and β-2:5-dimethylpiperazines described by Stoehr (*J. pr. Chem.*, 1893, [ii], **47**, 494; 1897, **55**, 49); these substances presumably have the constitution



$$\begin{matrix}CH_3\\H\end{matrix}>C<\begin{matrix}NH\cdot CH_2\\CH_2\cdot NH\end{matrix}>C<\begin{matrix}CH_3\\H\end{matrix},$$

and, as the last-named author points out, should be *cis*- and *trans*-isomerides. Stoehr further considered the possibility of compounds of the above constitution exhibiting optical activity, but concluded erroneously that the *trans*-isomeride should be resolvable into optically active isomerides; he was, however, unable to obtain either compound in an optically active form. In view of the importance of the type of stereoisomerism presented by substances of this class, we have subjected the α- and β-2:5-dimethylpiperazines to a careful examination with the object of resolving one isomeride into optically active components.

α-2:5-Dimethylpiperazine tartrate is used in pharmacy under the name of "lycetol," and Messrs. F. Bayer & Co., of Elberfeld, were so good as to provide us with such quantities of the residues obtained during the manufacture of this product as enabled us to separate considerable amounts of both the α- and β-2:5-dimethylpiperazine. It is not yet known which isomeride possesses the *cis*- and which the *trans*-configuration, and we expected to derive this information by the resolution of one of the two substances into optically active components; the resolvable form should possess the *cis*- or externally compensated configuration. An exhaustive series of fractional crystallisations of each base with several optically active acids was therefore undertaken, but no evidence was obtained indicating that resolution had been effected. An entirely new method was therefore devised for the resolution of externally compensated primary or secondary amines, a method which would not be expected to be rendered inapplicable by the possible formation of partly racemic compounds, but the application of this again led to no indication that either of the two dimethylpiperazines is resolvable into optically active components; the work thus carried out is described in the present paper. The failure of both kinds of method of resolution applied suggests that the isomerism of the α- and β-2:5-dimethylpiperazines is not of the type indicated by stereochemical theory; the further investigation of the whole subject is now being continued and developed on lines briefly indicated at the end of this paper.

α-2:5-*Dimethylpiperazine Tartrate*, $C_6H_{14}N_2,C_4H_6O_6,3H_2O$.

The following determinations of the rotation constants of lycetol and of sodium ammonium *d*-tartrate were made for purposes of comparison, the weight taken being made up to 30 c.c. with water and examined in a 4-dcm. tube at 20°:

	Lycetol (0·1650 gram).			$NaNH_4$-*d*-Tartrate (0·1310 gram).		
	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α.........	+0·45°	+0·41°	+0·40°	+0·47°	+0·41°	+0 40°
[α]	20·5	18·6	18·2	26·9	23·5	22·9
[M] ...	65·0	59·3	57·8	70·2	61·3	59·8
Rotatory dispersions:	1·125 ; 1·025.			1·175 ; 1·025.		

Considering that tartaric acid is a feeble dibasic acid, the molecular rotatory powers and the rotatory dispersions of the two salts agree so well as to afford no indication that lycetol contains an optically active base.

α-2:5-*Dimethylpiperazine*,

$$\begin{matrix}CH_3\\H\end{matrix}\!>\!C\!<\!\begin{matrix}NH\cdot CH_2\\CH_2\cdot NH\end{matrix}\!>\!C\!<\!\begin{matrix}CH_3\\H\end{matrix}.$$

The base separates on addition of concentrated potassium hydroxide to a strong aqueous solution of lycetol, and is readily purified by crystallisation first from warm benzene and afterwards from light petroleum; it exhibits the properties described by Stoehr, and is optically inactive in aqueous solution. It follows that no resolution into optically active components occurs during the technical preparation of the tartrate.

β-2:5-*Dimethylpiperazine.*

The residues obtained by Messrs. F. Bayer & Co. in the preparation of α-dimethylpiperazine consisted of a dark brown aqueous solution containing about 10 per cent. of dissolved matter. Addition of solid potassium hydroxide caused a separation into two liquid layers, and successive additions of the alkali ultimately caused the upper layer to become a pasty, crystalline mass; the latter was collected, and yielded on fractional distillation a quantity of base boiling at 160—170°, which solidified completely on cooling. By fractional crystallisation from light petroleum this product was separated into a sparingly soluble portion, α-dimethylpiperazine, and the much more readily soluble β-dimethylpiperazine; the identity of these two products with those described by Stoehr was established by the melting points and by preparation of the corresponding benzoyl derivatives.

α-2:5-*Dimethylpiperazine* d-*Bromocamphor-π-sulphonate*, $C_6H_{14}N_2,2C_{10}H_{14}OBr{\cdot}SO_3H$.

On evaporating an aqueous solution of α-2:5-dimethylpiperazine with two molecular proportions of *d*-α-bromocamphor-π-sulphonic acid on the water-bath, dissolving the gummy residue in a little hot alcohol, and allowing to cool in a desiccator, the salt is obtained in small, opaque, crystalline nodules. None of the salts with optically active acids, described in the present paper, gave a satisfactory melting point; some of them blacken at temperatures approaching 300°, and none melts sharply without decomposition:

0·1845 gave 0·2842 CO_2 and 0·0997 H_2O. C=42·01; H=6·05.

$C_{26}H_{44}O_8N_2Br_2S_2$ requires C=42·37; H=6·02 per cent.

As the result of careful fractional crystallisation from boiling alcohol a quantity of the salt was separated into four fractions exhibiting similar physical properties, and giving the following specific rotations respectively for the mercury-green line in a 1 per cent. aqueous solution at 20°: +90·8°, +90·4°, +90·5°, and +90·1°. 0·3255 Gram of the first fraction, made up to 30 c.c. with water at 20°, gave the following results in a 4-dcm. tube:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	+3·94°	+3·35°	+3·18°
[α]	90·8	77·2	73·3
[M]/2	334	284	269·5
[M] of NH_4-salt	346·5	295	279

The rotatory dispersions are, for $Hg_{green}/Na_{yellow}=1{\cdot}239$, and for $Hg_{yellow}/Na_{yellow}=1{\cdot}053$; the corresponding values for ammonium *d*-α-bromocamphor-π-sulphonate are 1·243 and 1·059. The latter values and the molecular rotatory powers of the ammonium salt stated above are taken from a previous paper (Pope and Read, Trans., 1910, **97**, 2201). The practical identity of the rotatory powers of the four fractions and the comparatively close correspondence between the rotation constants for the dimethylpiperazine and ammonium salts indicates that no resolution of the organic base into optically active components has occurred. This conclusion is confirmed by the fact that the dibenzoyl derivative prepared from the first fraction of salt is optically inactive and identical with that obtained from the original *α*-base.

The salt is readily soluble in hot alcohol, but sparingly so in cold; when left exposed to the air in contact with the absolute alcoholic mother liquor, it slowly absorbs water, and becomes converted into a gummy mass. The anhydrous salt is very soluble in water, and separates on spontaneous evaporation of the aqueous solution in large, square, transparent crystals, which contain water of crystallisation:

0·6039 lost 0·0544 in three hours at 100°. $H_2O = 9·01$.

$C_{26}H_{44}O_8N_2Br_2S_2,4H_2O$ requires $H_2O = 8·92$ per cent.

In a 1 per cent. aqueous solution at 20° the specific rotatory power for Hg_{green} was determined as $[\alpha] + 82·7°$, corresponding with $[M]/2 = +334°$; the latter value is identical with that found for the anhydrous salt.

During the fractional crystallisation of the salt from alcohol a small proportion of a very soluble substance crystallising in fine needles is usually obtained; this was identified as the corresponding salt of the *β*-base described below. It is difficult to entirely free the *α*-base from the *β*-isomeride, but the former may be obtained pure by crystallisation of the *d*-*α*-bromocamphor-*π*-sulphonate from alcohol as indicated above.

α-2:5-*Dimethylpiperazine* d-*Camphor-β-sulphonate*,
$C_6H_{14}N_2,2C_{10}H_{15}O \cdot SO_3H$.

On dissolving corresponding quantities of the base and acid in hot alcohol, and allowing the solution to cool, the salt separates in white needles. The compound is moderately soluble in hot alcohol, and very soluble in water; a quantity was fractionally crystallised from hot alcohol, and all the fractions were found to have the same specific rotatory powers. The following determinations were made with an aqueous solution containing 0·2296 gram in 30 c.c., the measurements being made at 20° in a 4-dcm. tube:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	+0·70°	+0·57°	+0·53°
$[\alpha]$	22·9	18·6	17·3
$[M]/2$	66·1	53·8	50·0
$[M]$ for the NH_4-salt ...	66·5	54·1	50·4

The rotatory dispersions are: $Hg_{green}Na/_{yellow} = 1·321$ and $Hg_{yellow}/Na_{yellow} = 1·076$; the corresponding values for the ammonium salt are 1·320 and 1·074. The molecular rotations of the organic salt are also practically identical with those for the ammonium salt stated above and quoted from Graham (this vol., p. 752):

0·1965 gave 0·3863 CO_2 and 0·1440. H=53·62; H=8·20.

$C_{26}H_{46}O_8N_2S_2$ requires C=53·93; H=8·02 per cent.

The benzoyl derivative prepared from the various fractions of the salt was inactive and identical with that of the original *α*-base.

α-2:5-*Dimethylpiperazine* d-*α*-*Bromocamphor*-*β*-*sulphonate*, $C_6H_{14}N_2,2C_{10}H_{14}BrO{\cdot}SO_3H,H_2O$.

The *d*-*α*-bromocamphor-*β*-sulphonic acid of Armstrong and Lowry (Trans., 1902, **81**, 1441) has been shown to be useful in the resolution of externally compensated tetrahydro-*p*-toluquinaldine (Pope and Beck, Trans., 1907, **91**, 458); the salt which it forms with *α*-dimethylpiperazine is, in marked contrast with those described above, only moderately soluble in cold water, and a considerable quantity of it was fractionally crystallised from this solvent. The various fractions are obtained in rosettes of hard, crystalline needles, and the salt contains an apparently indefinite proportion of water of crystallisation:

0·9321 lost 0·0369 in six hours at 100°. H_2O=3·96.

$C_{26}H_{44}O_8N_2Br_2S_2,H_2O$ requires H_2O=2·39 per cent.

0·1923 gave 0·2879 CO_2 and 0·1095 H_2O; after subtracting 3·96 per cent. H_2O, C=42·51; H=6·17.

$C_{26}H_{44}O_8N_2Br_2S_2$ requires C=42·37; H=6·02 per cent.

The several fractions into which the salt was separated by recrystallisation were found to have the same rotatory powers; the following is a typical set of determinations, and is stated together with values obtained with a carefully purified specimen of the calcium salt of the acid. The quantities of salt given were made up to 30 c.c. with water, and the solutions examined at 20° in 4-dcm. tubes.

	α-Dimethylpiperazine salt (0·2272 gram).				Calcium salt (0·2010 gram).		
	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α.........	+2·96°	+2·52°	+2·41°		+2·77°	+2·36°	+2·27°
[*α*]	97·7	84·2	79·6		103·4	88·1	84·7
[M]/2...	375	318	305	[M]	380	324	311
Rotatory dispersions:	1·228 ; 1·046.				1·220 ; 1·039.		

The determinations of the rotation constants of the various fractions of the salt thus afford no indication that resolution of the base has been effected; the base and the benzoyl derivative prepared from the salts also proved optically inactive.

The thorough investigation of the above salts indicated that the *α*-base could not be resolved by crystallisation with an optically active acid; the corresponding salts of the *β*-base were therefore prepared and examined.

β-Dimethylpiperazine d-*α-Bromocamphor-π-sulphonate*, $C_6H_{14}N_2,2C_{10}H_{14}BrO{\cdot}SO_3H$.

On prolonged fractional crystallisation of a quantity of this salt, prepared from β-base which has been carefully purified by crystallisation, a small quantity of salt of the α-base was separated, together with a number of identical fractions of salt of the β-isomeride. The latter salt separates from hot alcohol in small, colourless needles, and consecutive fractions, dried at 100°, gave the specific rotatory powers of +90·7°, +90·6°, +90·5°, +90·6°, and +90·7° respectively for the mercury-green line in aqueous solution. The following values were obtained with an aqueous solution containing 0·2026 gram in 30 c.c., and examined at 20° in a 4-dcm. tube:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	+2·45°	+2·08°	+1·97°
[α]	90·7	77·0	72·9
[M]/2	334	283	268

Rotatory dispersions: 1·244; 1·056.

0·1475 gave 0·2270 CO_2 and 0·0825 H_2O. C=41·97; H=6·26.

$C_{26}H_{44}O_8N_2Br_2S_2$ requires C=42·37; H=6·02 per cent.

The above experimental values for the rotation constants are practically identical with those obtained with the corresponding salt of the α-base, and indicate that no resolution of the base has been effected; the pure β-base and its benzoyl derivative prepared from the several fractions of salt proved optically inactive.

β-2:5-*Dimethylpiperazine* d-*Camphor-β-sulphonate.*

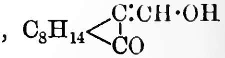
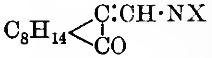
A quantity of this salt was prepared and separated, by fractional crystallisation from warm alcohol, into a number of fractions consisting of fine, colourless needles; the molecular rotatory powers of all the fractions differed inappreciably from the mean value of [M] +66·1° for the mercury-green line. Both base and benzoyl derivative prepared from the fractions were inactive, and, as it thus became clear that no resolution had been effected, the further characterisation of the salt was abandoned.

β-2:5-*Dimethylpiperazine* d-*α-Bromocamphor-β-sulphonate.*

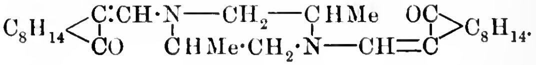
This salt is very soluble in water, and was fractionally crystallised from hot alcohol, from which solvent it is deposited in fine, colourless needles. The various fractions obtained varied more in molecular rotatory power than could be accounted for by error of measurement, and the variations were ultimately traced to the fact that the *d*-α-bromocamphor-β-sulphonic acid used contained a small quantity of an isomeride which is produced during the sulphonation; we have now accumulated a quantity of this isomeric acid, and are at present engaged in its further examination. In the case of each fraction, the base and the benzoyl derivative produced were optically inactive.

Just as in the case of the α-base, the attempt to resolve the β-base into optically active components by crystallisation with optically active acids proved unsuccessful; another type of method was therefore devised for the resolution of externally compensated bases, with results which are next described.

Condensation of d-*Oxymethylenecamphor with the* α- *and* β-2:5-*Dimethylpiperazines.*

We have previously shown (Trans., 1909, **95**, 171) that the readily obtainable *d*-oxymethylenecamphor can be conveniently used for the purpose of ascertaining whether a particular primary or secondary amine is externally compensated or potentially optically inactive; this substance, in its enolic form,  $C_8H_{14}<\begin{array}{l}C{:}CH\cdot OH\\ CO\end{array}$, reacts with secondary amines to form condensation products of the general type of constitution,  $C_8H_{14}<\begin{array}{l}C{:}CH\cdot NX\\ CO\end{array}$. If the original base, NHX, is externally compensated, it should yield two isomeric condensation products, whilst, if internally compensated or potentially inactive, only one such condensation product should be formed. After having found that no means of distinguishing the *cis*- from the *trans*-form of 2:5-dimethylpiperazine resulted from the examination of the salts which these bases form with optically active acids, we proceeded to apply the above-described condensation; this method likewise did not enable the necessary distinction to be made, because, as is shown below, the α- and β-2:5-dimethylpiperazines each yield but one condensation product.

α-2:5-*Dimethylpiperazino*-d-*methylenecamphor*,



$$C_8H_{14}<\begin{array}{ll}C{:}CH\cdot N{-\!\!-}CH_2{-\!\!-}CHMe & OC\\ CO\quad CHMe\cdot CH_2\cdot N{-\!\!-}CH{=}C & \end{array}>C_8H_{14}.$$

On warming a solution of α-2:5-dimethylpiperazine in 30 per cent. acetic acid with an alcoholic solution of two molecular proportions of *d*-oxymethylenecamphor on the water-bath, a considerable quantity of a crystalline substance separates; after collection of the latter and evaporating off most of the alcohol from the filtrate, a further quantity of the same substance may be obtained by neutralising the residue with sodium hydroxide solution. The crystalline solid separates from hot dilute alcohol, in which it is readily soluble, in soft, glistening plates, melting at 261°; prolonged fractional crystallisation from dilute alcohol resulted in the production of a number of fractions, which proved to be identical in composition, melting point, and rotatory power. A nearly theoretical yield is obtained, and the compound is soluble in most of the ordinary organic solvents:

0·1084 gave 0·3032 CO_2 and 0·0933 H_2O. C=76·36; H=9·63.
$C_{28}H_{42}O_2N_2$ requires C=76·64; H=9·66 per cent.

In the following determinations of rotatory power the weights of material stated were made up to 30 c.c. with the solvent and examined at 20° in 4-dcm. tubes:

Ethyl Alcohol.

	0·1004 gram.			0·2966 gram.		
	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α………	+10·28°	+8·67°	+8·25°	+30·16°	+25·48°	+24·17°
[α] ……	+768	+648	+616	+763	+644	+611
Rotatory dispersions:	1·246; 1·051.			1·248; 1·054.		

	Benzene (0·1049 gram).			*Pyridine* (0·1056 gram).		
α………	+9·19°	+7·80°	+7·44°	+9·88°	+8·38°	+7·94°
[α] ……	+657	+558	+532	+702	+595	+564
Rotatory dispersions:	1·235; 1·048.			1·244; 1·055.		

The solutions in the above solvents showed no mutarotation, but a solution of 0·1092 gram, made up to 30 c.c. with glacial acetic acid, exhibited very marked mutarotation; the observed rotatory power of this substance, at 20° in a 4-dcm. tube, was, for the mercury-green line, α+7·51° after ten minutes, and +3·18° after forty-eight hours, so that the rotatory power falls by more than 50 per cent. during two days' keeping. The following values were obtained with this solution after forty-eight hours:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α………………	+3·18°	+2·71°	+2·60°
[α] ……………	+218	+186	+178

Rotatory dispersions: 1·223; 1·042.

β-2:5-*Dimethylpiperazino*-d-*methylenecamphor.*

This substance was obtained in practically quantitative yield by the same method as was applied to the α-base; it separates from alcohol in glistening leaflets melting at 240°, and is more sparingly soluble in alcohol than the corresponding derivative of the α-base.

Careful fractional crystallisation of the material resulted in a number of fractions which had identical melting points and rotatory powers:

0·1070 gave 0·3002 CO_2 and 0·0925 H_2O. C = 76·52; H = 9·67.

$C_{28}H_{42}O_2N_2$ requires C = 76·64; H = 9·66 per cent.

The following determinations of rotatory power were made:

Ethyl Alcohol.

	0·1049 gram.			0·3097 gram.		
	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α …………	+10·86°	+9·14°	+8·71°	+32·00°	+26·98°	+25·62°
[α] …………	+776	+653	+623	+775	+653	+620

Rotatory dispersions: 1·247 ; 1·049. 1·249 ; 1·053.

	Benzene, 0·1111 gram.			*Pyridine*, 0·1049 gram.		
α………………	+9·91°	+8·39°	+8·00°	+9·85°	+8·35°	7·92°
[α] …………	+669	+556	+540	+704	+597	+566

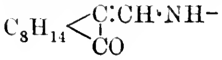
Rotatory dispersions: 1·239 ; 1·049. 1·244 ; 1·054.

The compound exhibited no mutarotation in the above solvents, but, just as with the isomeride, very marked mutarotation was observed with the acetic acid solutions. 0·1084 Gram, made up to 30·0 c.c. with glacial acetic acid, and examined at 20° in a 4-dcm. tube, gave an observed rotation for the mercury-green line of α +5·18° ten minutes after the solution was made up; this value fell gradually to α +2·34° after forty-eight hours. The values obtained after forty-eight hours' keeping are as follows:

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α …………	+2·34°	+2·00°	+1·93°
[α]…………	+162	138	134

Rotatory dispersions: 1·212 ; 1·036.

The results described above prove that *d*-oxymethylenecamphor yields but one condensation product with each of the two isomeric 2:5-dimethylpiperazines, and are hence quite at variance with what stereochemical theory would lead us to anticipate. Further, the two condensation products exhibit very similar properties; their rotation constants do not differ greatly, and each exhibits a remarkable mutarotation in acetic acid solution. We have previously observed that the *d*-oxymethylenecamphor derivatives of primary amines exhibit mutarotation in a variety of solvents, and have attributed this to the occurrence of isodynamic isomerism which is rendered possible by the presence of the grouping



$$C_8H_{14}<\begin{matrix}C{:}CH{\cdot}NH{-}\\ |\\ CO\end{matrix}$$

in the normal constitution attributable to such derivatives (Trans., 1909, **95**, 171); the exhibition of mutarotation by the *d*-oxymethylenecamphor derivatives of the α- and β-2:5-dimethylpiperazines, secondary bases which can hardly lead to the formation of condensation products containing the group –NH–, thus appeared in contradiction with our previous results, and the interpretation of them which we advanced. It is striking that the *d*-oxymethylenecamphor derivatives of the two dimethylpiperazines now described only exhibit mutarotation in acetic acid solution, whilst the corresponding derivatives of primary bases show mutarotation in neutral solvents.

The explanation of the apparent anomaly seems to lie in the following observation. Both dimethylpiperazino-*d*-methylenecamphors dissolve readily in cold concentrated hydrochloric acid, and, after a short time, *d*-oxymethylenecamphor crystallises from the solution. Since this decomposition occurs rapidly in contact with cold hydrochloric acid, it is to be anticipated that in glacial acetic acid solution the condensation products would hydrolyse more slowly with formation of *d*-oxymethylenecamphor and the original dimethylpiperazine. In this connexion it is interesting to note that anilino-*d*-methylenecamphor undergoes no change when boiled with concentrated hydrochloric acid.

In a previous paper we have noted that we were unable to apply the condensation products of *d*-oxymethylenecamphor to the resolution of externally compensated bases because we were not acquainted with any mode in which the original base could be recovered from the condensation product; the similarity of the condensation products obtained with the α- and β-dimethylpiperazines made it necessary, however, that the original α- and β-base should be so recovered, and we have therefore worked out a method by means of which this recovery may be quantitatively effected.

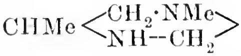
On adding to a carbon tetrachloride solution of either α- or β-2:5-dimethylpiperazino-*d*-methylenecamphor a carbon tetrachloride solution of two molecular proportions of bromine, immediate decolorisation occurs, and an orange-yellow, crystalline substance is precipitated; this is doubtless the tetrabromide of the condensation product, but as it could not be recrystallised from any convenient solvent without decomposition it was not analysed; its weight, however, corresponds with a theoretical yield of the tetrabromide. It dissolves readily in hot alcohol, and, after heating with alcohol on the water-bath until the colour disappears, and allowing to cool, the hydrobromide of the α- or β-2:5-dimethylpiperazine is deposited in quantitative yield. The condensation product obtained from the α-dimethylpiperazine thus furnishes the hydrobromide, which crystallises from alcohol in colourless needles melting at 307°; as this substance was found to contain water of crystallisation, contrary to the indications given by Stoehr, it was fully analysed:

0·6689 lost 0·0304 at 100°. $H_2O=4·54$.
0·1107 gave 0·1001 CO_2 and 0·0618 H_2O. $C=24·66$; $H=6·25$.
0·1892 required 13·0 c.c. $N/10$-$AgNO_3$. $Br=54·91$.
$C_6H_{16}N_2Br_2+4·54$ per cent. H_2O requires $C=24·91$; $H=6·07$; $Br=55·29$ per cent.

On applying the same process to the condensation product obtained from *β*-2:5-dimethylpiperazine, the hydrobromide of the latter was deposited in small, glistening scales, which do not melt at 310°; the salt does not take up water of crystallisation, and does not lose weight at 110°:

0·1302 gave 0·1227 CO_2 and 0·0706 H_2O. $C=25·70$; $H=6·07$.
0·1194 required 8·6 c.c. $N/10$-$AgNO_3$. $Br=57·56$.
$C_6H_{16}N_2Br_2$ requires $C=26·09$; $H=5·84$; $Br=57·92$ per cent.

All the samples of the hydrobromides of the *α*- and *β*-dimethylpiperazines obtained as just described above are optically inactive in aqueous solution; it may also be noted that, on evaporating the alcoholic solutions from which these salts are deposited and crystallising the residue by the addition of an appropriate amount of water, *d*-bromo-oxymethylcamphor is obtained; and that the hydrobromides of the *α*- and *β*-bases may be obtained directly by adding the requisite quantity of bromine to the cold alcoholic solution of the condensation product. In this case, however, care must be taken not to add an excess of bromine, as this leads to the precipitation of a perbromide of the base.

It has been shown above that, contrary to expectation, neither of the two 2:5-dimethylpiperazines is resolvable into optically active components; we propose now to study further the anomaly which has been pointed out in the following manner: 2:5-Dimethylpyrazine,  $CMe{<}\begin{matrix}CH\cdot N\\ N{:}CH\end{matrix}{>}CMe$, yields a monomethiodide; this on reduction should yield the *cis*- and *trans*-1:2:5-trimethylpiperazines,  $CHMe{<}\begin{matrix}CH_2\cdot NMe\\ NH\text{--}CH_2\end{matrix}{>}CHMe$, which it is proposed to resolve by the aid of an optically active acid into optically active components. Four optically active bases should thus result, which will combine with methyl iodide yielding *d*- and *l*-*cis*-1:2:4:5-tetramethylpiperazine and their internally compensated *trans*-isomeride; the externally and internally compensated tetramethylpiperazines corresponding with these should be formed by the action of methyl iodide on *α*- and *β*-2:5-dimethylpiperazines, and it should hence be possible to ascertain which of the latter has the *cis*- and which the *trans*-configuration.

Incidentally, during this investigation, a very convenient method has been devised for resolving externally compensated primary and secondary amines by the aid of their condensation products with *d*-oxymethylenecamphor; we are at present engaged on the further application of this method, and have already found that it can be very satisfactorily applied to the resolution of such externally compensated bases.

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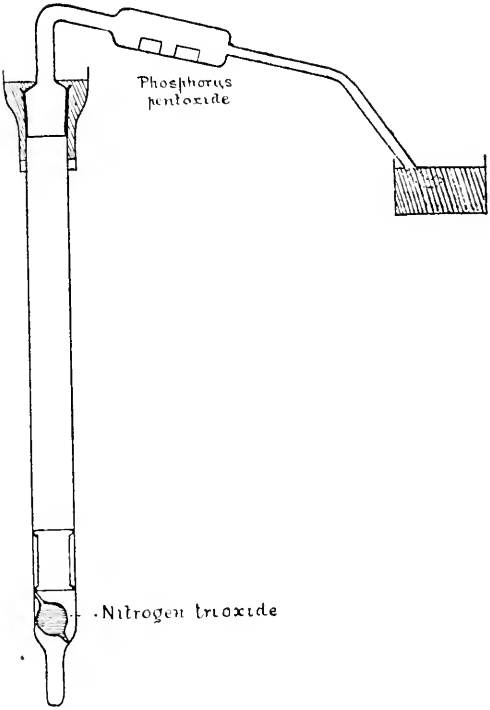
CCXLVI.—*The Change in the Boiling Points of the Trioxide and Tetroxide of Nitrogen on Drying*

By HERBERT BRERETON BAKER and MURIEL BAKER.

IN consequence of a private communication from Prof. A. Smith with regard to the volatility of dried calomel, a search was made through our old laboratory note-books to see if any abnormalities in the vaporisation of dried substances had been recorded. None was found in regard to ammonium chloride or calomel, but among the determinations of the vapour density of nitrogen trioxide two instances had been noticed in which this substance, carefully dried, had failed to boil at +15°, the ordinary boiling point being −2°. In Prof. Smith's interesting work on calomel, the drying had been more complete than in the investigation carried out by one of us on that substance, and it was thought worth while to determine the boiling point of very dry nitrogen trioxide. It fortunately happened that we had kept, as a lecture exhibit, a tube with the attached series of bulbs, in which the liquid trioxide had been sealed up with phosphoric oxide for three years. The trioxide was distilled into the bulbs by cooling the latter with liquid air, and in this way it was divided by sealing the capillary tubes between the bulbs into three portions. These sealed bulbs were dried on the outside by allowing them to remain in a desiccator over phosphoric oxide. For the determination of the boiling point a Jena-glass tube was used about 40 cm. in length and 15 cm. in internal diameter. Into one end was ground a hollow glass stopper, which opened into a wide tube containing phosphoric oxide, this tube being drawn out into a long capillary about 2 mm. in diameter. The other end of the

Jena tube was drawn out so that its internal diameter was about 8 mm., its wall being as thin as was consistent with safety. After drying by heating in a current of air dried by phosphoric oxide, a bulb of nitrogen trioxide was introduced. A piece of Jena-glass rod was placed above the bulb containing the dried liquid so as to facilitate the fracture of the bulb. The tube was filled with nitrogen dried by phosphoric oxide, and kept for three months, the ground joint being protected by a mercury seal. At the end of this time a thermometer was bound to the thin end of the tube,



and the capillary end of the phosphoric oxide tube was broken under previously dried mercury. The bulb was broken while the tube was surrounded by melting ice, and no boiling was perceptible. The temperature of the bath was allowed to rise, and the liquid was found not to boil until a temperature of 43° was reached. A second experiment indicated a boiling point of 42·5°. The vapour of the very dry trioxide was red, and on cooling to +10° it condensed to the green liquid, which on further cooling turned bright blue, showing that it was still nitrogen trioxide.

On allowing some nitrogen, dried by passage through a long column of phosphoric oxide, to enter the tube, the small amount of moisture it contained caused rapid dissociation, and the resulting sudden increase of pressure blew out the stopper of the tube.

A similar experiment was tried with a specimen of nitrogen tetroxide which had been drying for over a year. The amount of liquid available unfortunately was small, less than 1 c.c. On raising the temperature the liquid was apparently unchanged at 22°, the ordinary boiling point. Further heating of the bath produced evaporation, but at 69° the liquid was still visible, and not in a state of ebullition. Above this temperature the liquid, which was orange-red in colour, disappeared. The pressure in each of the three experiments was 757 mm.

The explanation of these abnormal boiling points is probably to be found in the difference of complexity in the liquids. It is likely that the liquid nitrogen trioxide has a more complex molecule than that represented by the formula N_2O_3; in fact, in one of our former experiments a vapour density was obtained, which indicated a mixture of three molecules of N_4O_6 to one molecule of N_2O_3 (Trans., 1907, **91**, 1862). It may be supposed that a liquid consisting of more complex molecules would have a higher boiling point than one of simpler constitution, and that the almost complete absence of water would enable the complex liquid to boil as such. It is possible that a more complex molecule exists in the liquid below $-2°$, since at this temperature a marked change in colour takes place from olive-green to bright blue. It may be worthy of remark that a flat bulb containing this liquid, which had been used to show this change of colour at the reading of our former paper, has, during the five years' contact with phosphoric oxide, acquired a bright blue colour, which is permanent at the ordinary temperature.

Further experiments are in progress to determine the boiling points of dried liquids, in order to see if the dissociability of the vapours is an essential condition for the raising of the boiling points.

The work was carried out in the laboratory of Christ Church, Oxford.

Imperial College of Science and Technology,
London, S.W.

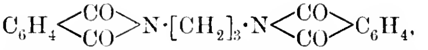
CCXLVII.—2-*Phenyl*-1 : 4 : 5 : 6-*tetrahydropyrimidine and Benzoyl-αγ-diaminopropane.*

By Gerald Eyre Kirkwood Branch and
Arthur Walsh Titherley.

In the synthesis of hexahydropyrimidine derivatives, to be described in a subsequent paper, it was desired to start with the monobenzoyl derivative of αγ-diaminopropane,

$$NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NHBz,$$

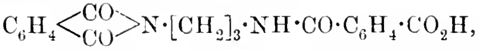
and submit it to the action of formaldehyde. Numerous unsuccessful attempts to obtain this compound, which has not been described, were made, and it is proposed to define these briefly, together with a final attempt which was successful, in which 2-phenyl-1 : 4 : 5 : 6-tetrahydropyrimidine was used. In the earlier attempts Gabriel and Weiner's αγ-diphthaliminopropane (*Ber.*, 1888, **21**, 2669),



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}N\cdot[CH_2]_3\cdot N{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_4,$$

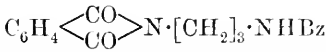
was used as a starting point, the intention being to submit the compound to half-hydrolysis and obtain monophthalyl-αγ-diaminopropane. By benzoylation of this compound and subsequent elimination of the phthalyl residue, by alkali- and then acid-hydrolysis, monobenzoyl-αγ-diaminopropane should be obtained. With this end in view the diphthalyl derivative was converted by Gabriel and Weiner's method (*loc. cit.*) into trimethylenediphthalamic acid, $CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot[CH_2]_3\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$.

The latter compound was found to be extremely sensitive to acid-hydrolysis, but although many trials were made under varying conditions it was never found possible to eliminate phthalic acid in two stages. Even on heating with water ready hydrolysis occurs, but both phthalic groups are split off. The next attempt made was to eliminate one molecule of water and to obtain α-phthaliminopropyl-γ-phthalamic acid,



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}N\cdot[CH_2]_3\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H,$$

with the object of submitting this to acid-hydrolysis, since it was found that the phthalimino-group, unlike the phthalamic residue, was very resistant to acid-hydrolysis, although sensitive to alkaline agents (with ring rupture only). Trimethylenediphthalamic acid was accordingly submitted cautiously to the influence of heat and dehydrating agents, but in all cases, even under very carefully moderated conditions, two molecules of water were eliminated, yielding the original diphthalimino-derivative, and this was true also when a comparatively small proportion of the total number of molecules were dehydrated. Conversely, attempts to prepare the desired monobasic acid by alkali-fission of one of the phthalimino-rings, even under carefully moderated and very varied conditions, never yielded anything but the diphthalamic acid derivative produced by fission of both rings, and this was true also when the action had proceeded to a comparatively slight extent. It became obvious from the above negative results that if the attempted reactions, as may be supposed, take place in two successive stages, it is impossible even partly to restrict the action to the first stage, because the velocity of the second action must be greatly higher than that of the first. Attempts, which were next made, to prepare the compound



$$\mathrm{C_6H_4}\Big\langle\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}\Big\rangle\mathrm{N\cdot[CH_2]_3\cdot NHBz}$$

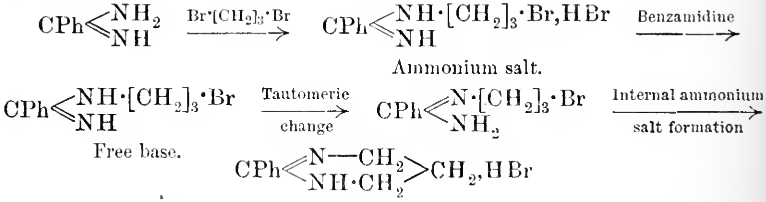
by the action of sodium benzamide on γ-bromopropylphthalimide proved equally unsuccessful.

The authors therefore turned next to the benzoylation of αγ-diaminopropane with the object of obtaining the monobenzoyl derivative, but here again the same difficulty referred to presented itself, and in spite of every precaution the dibenzoyl derivative, $\mathrm{NHBz\cdot[CH_2]_3\cdot NHBz}$, described by Strache (*Ber.*, 1888, **21**, 2365) in a pure form always resulted. That is using 1 mol. of benzoyl chloride or benzoic anhydride and 1 mol. of αγ-diaminopropane, the *s*-dibenzoyl derivative results, and half of the diamine remains unaffected. This is probably to be explained in the case of the Schotten-Baumann reaction by the fact that since benzoylation takes place strictly in the oil (benzoyl chloride) and not in the aqueous phase, the concentration of the benzoyl chloride is at all moments of the reaction relatively very high. This explanation, however, cannot hold good in the case of other unsuccessful attempts made, when pyridine and acetone were used as solvents. Similarly, it was found impossible to obtain monobenzoyl-αγ-diaminopropane by heating the monobenzoate of αγ-diaminopropane. Lastly an attempt was made to obtain it by treating the monoacetate of αγ-diaminopropane with benzaldehyde, benzoylating the resulting condensation derivative (after liberating the base from its acetate), and then cautiously hydrolysing to eliminate benzaldehyde. Nothing definite could be obtained in this way. The authors next turned to 2-phenyl-1:4:5:6-tetrahydropyrimidine (I) in the hope of effecting hydrolytic fission of the ring giving monobenzoyl-αγ-diaminopropane (II), thus:

$$\mathrm{CPh}\Big\langle\begin{matrix}\mathrm{NH\cdot CH_2}\\\mathrm{N{-\!-}CH_2}\end{matrix}\Big\rangle\mathrm{CH_2}\longrightarrow\mathrm{COPh\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2}$$

(I.) (II.)

2-Phenyl-1 : 4 : 5 : 6-tetrahydropyrimidine (I) has been already described in an impure form as an oil by Pinner (*Ber.*, 1893, **26**, 2122), who obtained it by the condensation of benzamidine and $\alpha\gamma$-dibromopropane, which were allowed to react in ether–alcohol solution at 40° for several weeks. The same compound is also mentioned by Hofmann (*Ber.*, 1888, **21**, 2337), who states that it is produced by heating dibenzoyl-$\alpha\gamma$-diaminopropane in hydrogen chloride, but he gives an unsatisfactory account of its isolation and properties. The authors have repeated Hofmann's work, and have failed to obtain the compound in this way, and it is evident that the substance described by Hofmann was obtained only in very small yield. It would appear that both Pinner's and Hofmann's products contained 2-phenyl-1 : 4 : 5 : 6-tetrahydropyrimidine, since each obtained correct values for the analysis of the platinum double salt. Pinner, in the condensation referred to above, obtained as the main product of the reaction apparently bromopropylbenzamidine, $\mathrm{CPh(:NH)\cdot NH\cdot[CH_2]_3\cdot Br}$, which crystallised out incompletely on keeping, leaving an oil which could not be fractionated, but consisted largely of 2-phenyl-1 : 4 : 5 : 6-tetrahydropyrimidine, and this appears to be the purest form in which this compound has hitherto been obtained. The authors have cleared up the doubt concerning the compound by synthesising the pure substance by a modification of Pinner's method, acting on the following principles. The reaction between benzamidine and $\alpha\gamma$-dibromopropane evidently takes place in successive stages, which may be represented thus:



$$\mathrm{CPh}{\lessdot}\genfrac{}{}{0pt}{}{\mathrm{NH_2}}{\mathrm{NH}} \xrightarrow{\mathrm{Br\cdot[CH_2]_3\cdot Br}} \mathrm{CPh}{\lessdot}\genfrac{}{}{0pt}{}{\mathrm{NH\cdot[CH_2]_3\cdot Br,HBr}}{\mathrm{NH}} \xrightarrow{\text{Benzamidine}}$$

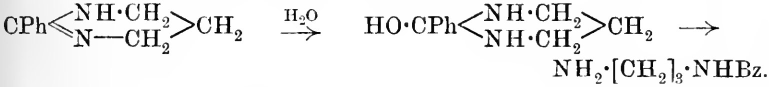
Ammonium salt.

$$\mathrm{CPh}{\lessdot}\genfrac{}{}{0pt}{}{\mathrm{NH\cdot[CH_2]_3\cdot Br}}{\mathrm{NH}} \xrightarrow[\text{change}]{\text{Tautomeric}} \mathrm{CPh}{\lessdot}\genfrac{}{}{0pt}{}{\mathrm{N\cdot[CH_2]_3\cdot Br}}{\mathrm{NH_2}} \xrightarrow[\text{salt formation}]{\text{Internal ammonium}}$$

Free base.

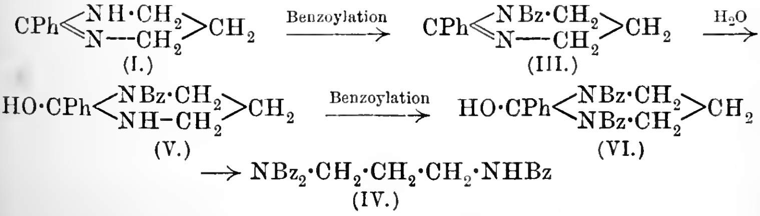
$$\mathrm{CPh}{\lessdot}\genfrac{}{}{0pt}{}{\mathrm{N{-}CH_2}}{\mathrm{NH\cdot CH_2}}{>}\mathrm{CH_2,HBr}$$

The first stage is that of ordinary ammonium salt formation. The free base (incompletely liberated by the action of benzamidine present) can only undergo internal ammonium salt formation (leading to the tetrahydropyrimidine derivative) after tautomeric change. Except the latter, these reactions are of low (and unknown) velocity, which, however, would probably, like the ordinary Hofmann ammonium salt synthesis, be accelerated by alcohol. In view of these considerations it is clear that, in the synthesis of 2-phenyl-1 : 4 : 5 : 6-tetrahydropyrimidine, 2 mols. of benzamidine for 1 mol. of $\alpha\gamma$-dibromopropane are necessary. With smaller quantities of benzamidine or insufficient time, the hydrobromide of ω-bromopropylbenzamidine must remain. In practice these relative proportions were used in boiling alcohol for three days. It was found, however, that although the desired reaction was practically complete, the final yield of 2-phenyl-1:4:5:6-tetrahydropyrimidine was very small. This was partly due to secondary changes, such as the formation of allyl bromide, and slow decomposition of benzamidine by alcohol and traces of moisture which could not be excluded, giving ethyl benzoate and benzamide. Further, the extremely slow and laborious nature of the subsequent operations necessary to isolate the cyclic base tends to diminish the yield. The base is present in the reaction mixture, as its hydrobromide, together with benzamidine hydrobromide, and great difficulty was encountered in separating the two. 2-Phenyl-1:4:5:6-tetrahydropyrimidine when finally obtained in a pure condition is a crystalline solid, which becomes oily on treatment with water, and dissolves in excess. When heated with dilute ammonia at 80° it slowly takes up water, and passes into monobenzoyl-$\alpha\gamma$-diaminopropane, probably on the following mechanism, which is similar to that described by one of the authors in the similar decomposition of 2-phenyl-1:3-benzoxazine-4-one (Titherley, Trans., 1910, **97**, 201):



$$\mathrm{CPh}\left\langle\begin{matrix}\mathrm{NH\cdot CH_2}\\ \mathrm{N{-}CH_2}\end{matrix}\right\rangle\mathrm{CH_2} \xrightarrow{\mathrm{H_2O}} \mathrm{HO\cdot CPh}\left\langle\begin{matrix}\mathrm{NH\cdot CH_2}\\ \mathrm{NH\cdot CH_2}\end{matrix}\right\rangle\mathrm{CH_2} \longrightarrow \mathrm{NH_2\cdot[CH_2]_3\cdot NHBz}.$$

The resulting open-chain base, which is a crystalline solid readily soluble in water, may be isolated through its oxalate. Its constitution follows from the fact that on hydrolysis it yields benzoic acid and $\alpha\gamma$-diaminopropane, whilst on benzoylation it yields dibenzoyl-$\alpha\gamma$-diaminopropane, identical with that obtained directly from $\alpha\gamma$-diaminopropane. The benzoylation of 2-phenyl-1:4:5:6-tetrahydropyrimidine by the Schotten-Baumann method gave unexpected results. Instead of the monobenzoyl derivative (III), tribenzoyl-$\alpha\gamma$-diaminopropane (IV) is produced, and, so far, the compound III has not been obtained. This anomalous reaction is readily intelligible if it is assumed that the monobenzoyl derivative (III), first formed, is very sensitive to water in presence of alkali (compare the behaviour of 2-phenyl-1:3-benzoxazine-4-one with acids); the intermediate compound (V) produced by addition of water being benzoylated, thus yields the compound VI, which is the cyclic tautomeric form of tribenzoyl-$\alpha\gamma$-diaminopropane (IV):



$$\underset{\text{(I.)}}{\mathrm{CPh}\left\langle\begin{matrix}\mathrm{NH\cdot CH_2}\\ \mathrm{N{-}CH_2}\end{matrix}\right\rangle\mathrm{CH_2}} \xrightarrow{\text{Benzoylation}} \underset{\text{(III.)}}{\mathrm{CPh}\left\langle\begin{matrix}\mathrm{NBz\cdot CH_2}\\ \mathrm{N{-}CH_2}\end{matrix}\right\rangle\mathrm{CH_2}} \xrightarrow{\mathrm{H_2O}}$$

$$\underset{\text{(V.)}}{\mathrm{HO\cdot CPh}\left\langle\begin{matrix}\mathrm{NBz\cdot CH_2}\\ \mathrm{NH{-}CH_2}\end{matrix}\right\rangle\mathrm{CH_2}} \xrightarrow{\text{Benzoylation}} \underset{\text{(VI.)}}{\mathrm{HO\cdot CPh}\left\langle\begin{matrix}\mathrm{NBz\cdot CH_2}\\ \mathrm{NBz\cdot CH_2}\end{matrix}\right\rangle\mathrm{CH_2}}$$

$$\longrightarrow \underset{\text{(IV.)}}{\mathrm{NBz_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NHBz}}$$

EXPERIMENTAL.

The experiments 1—8 described below refer to the attempts which were carried out with a view to the synthesis of benzoyl-$\alpha\gamma$-diaminopropane.

(1) *Hydrolysis of Trimethylenediphthalamic Acid.*

Acid hydrolysis, even when cautiously carried out, invariably gave phthalic acid and $\alpha\gamma$-diaminopropane. By heating 0·5 gram of trimethylenediphthalamic acid with 5 c.c. of water at 100° for four minutes, 20 per cent. was hydrolysed, yielding $\alpha\gamma$-diaminopropane phthalate. The experiment was modified as to time, temperature, and concentration, but in no case was the desired γ-aminopropyl-α-phthalamic acid formed.

(2) *Dehydration of Trimethylenediphthalamic Acid.*

On heating at 100° in the air, until the loss in weight corresponded with 1 mol. of water, a semi-solid fusion was obtained, which, however, consisted of unchanged substance and diphthalyl-$\alpha\gamma$-diaminopropane, melting at 198°.

The action of acetyl chloride, both free and in benzene solution, and of acetic anhydride in acetic acid solution, under various conditions gave only diphthalyl-$\alpha\gamma$-diaminopropane.

(3) *Action of Alkali on Diphthalyl-$\alpha\gamma$-diaminopropane.*

Half a gram of diphthalyl-$\alpha\gamma$-diaminopropane in 75 c.c. of alcohol at 80° was treated cautiously (drop by drop) with one equivalent of $N/10$-aqueous potassium hydroxide in the presence of phenolphthalein, so that the concentration of free alkali was always kept as low as possible. The alkali was fairly rapidly taken up, but rupture of both phthalimino-rings had occurred, giving the potassium salt of trimethylenediphthalamic acid, which after isolation melted at 94°, and leaving nearly 0·25 gram of unchanged diphthalyl-$\alpha\gamma$-diaminopropane.

(4) *Action of Benzoyl Chloride on Trimethylenediphthalamic Acid.*

Several experiments were carried out at 60° and at 120° with different proportions of the reacting substances. Hydrogen chloride was given off, and diphthalyl-$\alpha\gamma$-diaminopropane (m. p. 198°), together with $\alpha\gamma$-diaminopropane hydrochloride, were found, but no benzoylphthalyl-$\alpha\gamma$-diaminopropane.

(5) *Action of Sodium Benzamide on γ-Bromopropylphthalimide.*

Equivalent quantities were heated at 125—130° for an hour. Free benzamide and sodium bromide were formed in quantity, together apparently with phthalylallylamine, which, however, was not investigated. No benzoylphthalyl-αγ-diaminopropane was formed.

(6) *Benzoylation of αγ-Diaminopropane.*

By the Schotten-Baumann method, using one equivalent of benzoyl chloride, only half the diamine reacted, giving the dibenzoyl derivative (m. p. 151°). The same compound resulted by benzoylation in pyridine solution with benzoic anhydride, also by benzoylation of αγ-diaminopropane monobenzoate or monohydrochloride in acetone solution with benzoic anhydride. In all cases, using one equivalent of benzoic anhydride, half the diamine remained unaffected, and the remainder gave the dibenzoyl derivative.

(7) *Action of Heat on αγ-Diaminopropane Monobenzoate.*

At 170—180° for six hours darkening occurred, but no monobenzoyl-αγ-diaminopropane could be isolated from the product.

(8) *Condensation of αγ-Diaminopropane Monoacetate and Benzaldehyde.*

The reaction was carried out in alcoholic solution, and a discoloured, viscid syrup was obtained after evaporation. This syrup, which is probably the impure acetate of benzylidene-αγ-diaminopropane, has not been further investigated, but attempts to benzoylate it in pyridine and subsequently eliminate benzaldehyde by acid hydrolysis, in order to obtain monobenzoyl-αγ-diaminopropane, were unsuccessful.

Condensation of Benzamidine and αγ-Dibromopropane.

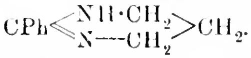
After several trials the following method gave the best results:

Forty-five grams of benzamidine hydrochloride in the minimum quantity of water were treated at 0° with the equivalent amount of 50 per cent. aqueous potassium hydroxide. The solution was then made into a thin paste with an excess of anhydrous potassium carbonate, and the free benzamidine extracted several times with alcohol (about 200 c.c.). The alcoholic solution, after drying with anhydrous potassium carbonate, was heated to boiling in a reflux apparatus with 23·4 grams of αγ-dibromopropane for three days.

The alcohol was removed from the product at the ordinary temperature in a vacuum, and the semi-solid mass remaining, consisting essentially of the hydrobromides of benzamidine and 2-phenyl-1:4:5:6-tetrahydropyrimidine, was treated with water and extracted with ether. The ethereal extract yielded about 2·5 grams of a mixture of benzamide and ethyl benzoate.

The aqueous solution was then treated in the cold with excess of 50 per cent. aqueous potassium hydroxide, and the yellow oil produced was extracted with benzene. The benzene was removed in a vacuum, and the mixed bases remaining were neutralised exactly (using litmus) with aqueous oxalic acid. The aqueous solution after filtering from benzamide (1·8 grams) was concentrated in the cold over sulphuric acid in a vacuum. The residual mass of syrup and crystals (normal oxalates) weighing 35 grams was extracted with alcohol, and the insoluble benzamidine oxalate collected. The alcohol filtrate was again evaporated, and, as before, the residue once more extracted with alcohol, and the insoluble benzamidine oxalate separated. In this way most of the benzamidine was removed as insoluble oxalate (total weight 20·6 grams), whilst the oxalate of the cyclic base remained in solution. The latter on evaporation remained as a syrup, which crystallised only with difficulty. It was therefore converted into the hydrogen oxalate by treatment with an excess of anhydrous oxalic acid in acetone solution, when the hydrogen oxalate of the cyclic base separated as a white, crystalline solid (5·7 grams). The mother liquor still contained small quantities in solution, which were not recovered, together with benzamidine oxalate, and these were precipitated in syrupy form on adding more acetone. This syrup on decomposition with hot dilute aqueous ammonia gave 0·5 gram of benzamide and 0·6 gram of monobenzoyl-αγ-diaminopropane (p. 2350), which was isolated as its oxalate.

2-*Phenyl*-1:4:5:6-*tetrahydropyrimidine*,



$$\mathrm{CPh}\left<\begin{matrix}\mathrm{NH{\cdot}CH_2}\\ \mathrm{N{-}{-}CH_2}\end{matrix}\right>\mathrm{CH_2}.$$

The free base was isolated from the hydrogen oxalate, described above, by treating its saturated solution in water with 50 per cent. aqueous potassium hydroxide and extracting the oil with a small quantity of ether. The dried ethereal solution was deprived of ether at 20° by a current of pure dry air, when the base remained as a colourless oil, which rapidly set to a solid, white, crystalline mass melting at 72—78°:

0·1433, by Kjeldahl's method, required 18·0 c.c. *N*/10-HCl. N = 17·58.

$C_{10}H_{12}N_2$ requires N = 17·50 per cent.

2-*Phenyl*-1 : 4 : 5 : 6-*tetrahydropyrimidine* is readily soluble in ether or benzene, and excessively so in alcohol. With a small quantity of water it changes to an oil, which dissolves in about fifty parts of water, giving a strongly alkaline solution, which on spontaneous evaporation in air leaves a crystalline carbonate. On heating with dilute aqueous ammonia, the cyclic base slowly passes into monobenzoyl-$\alpha\gamma$-diaminopropane (see p. 2350).

The *hydrochloride* crystallises slowly in long, colourless prisms from the syrup obtained on allowing its aqueous solution to evaporate in the air.

The *nitrate* crystallises readily on evaporating its aqueous solution.

The *picrate* separates from aqueous solutions as a microcrystalline, yellow precipitate.

The *platinichloride* separates from an aqueous solution as a microcrystalline powder, which melts and decomposes at 213—214°. For analysis it was dried at 100°:

0·0879 gave 0·0233 Pt. Pt = 26·52.

$(C_{10}H_{12}N_2,HCl)_2PtCl_4$ requires Pt = 26·66 per cent.

The *oxalate* on evaporating its aqueous solution prepared from the base, remains as a syrup, which slowly crystallises in a vacuum and melts at 175°. It is readily soluble in alcohol, and excessively soluble in water.

The *hydrogen oxalate* (described above) melts at 180°, and is very soluble in water, and moderately so in alcohol.

Benzoylation of 2-*Phenyl*-1 : 4 : 5 : 6-*tetrahydropyrimidine : Tribenzoyl-$\alpha\gamma$-diaminopropane*, $NBz_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NHBz$.

By the Schotten-Baumann method the pyrimidine base is readily benzoylated, but takes up two molecules of benzoyl chloride, and the ring is broken. An oil was obtained, which solidified on keeping. After recrystallisation from benzene and light petroleum, and finally from aqueous alcohol, colourless needles were obtained melting at 144°:

0·1980, by Kjeldahl's method, required 10·6 c.c. *N*/10-HCl. N = 7·49.

0·0776, by Kjeldahl's method, required 4·0 c.c. *N*/10-HCl. N = 7·22.

$C_{24}H_{22}O_3N_2$ requires N = 7·25 per cent.

The constitution of the compound follows from the fact that on cautious hydrolysis with 10 per cent. aqueous alkali at 100° for thirty-five minutes, it yields benzoic acid and dibenzoyl-$\alpha\gamma$-diaminopropane. The latter melted at 150°, and a mixture with a pure specimen obtained from $\alpha\gamma$-diaminopropane melted at 150°. Attempts to confirm the fact that the compound melting at 144° is tribenzoyl-$\alpha\gamma$-diaminopropane by pyridine benzoylation of dibenzoyl-$\alpha\gamma$-diaminopropane failed, because the latter, probably from steric causes, was not benzoylated even after eight days, and the unchanged material was entirely recovered. Tribenzoyl-$\alpha\gamma$-diaminopropane is soluble in cold alcohol, although less so than the dibenzoyl derivative. It is readily soluble in benzene, but sparingly so in ether.

Monobenzoyl-$\alpha\gamma$-diaminopropane, $NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NHBz$.

In the synthesis of this base, through 2-phenyl-1:4:5:6-tetrahydropyrimidine, the actual isolation of the latter was not found to be necessary, and the following treatment was adopted:

An alcoholic solution of benzamidine from 10 grams of the hydrochloride was heated as described above with 5·2 grams of $\alpha\gamma$-dibromopropane for three days. The alcohol was removed from the product at the ordinary temperature in a vacuum, the syrupy residue consisting chiefly of the hydrobromides of 2-phenyl-1:4:5:6-tetrahydropyrimidine and benzamidine, was treated with a little water and freed from impurities (benzamide and ethyl benzoate) by extracting three times with ether. The aqueous solution was then treated with excess of 50 per cent. potassium hydroxide, and the oily mixed bases were extracted twice with benzene. After remaining over solid potassium hydroxide, the benzene was removed at the ordinary temperature in a vacuum, leaving a brown oil (8·3 grams). In order to remove as much benzamidine as possible the oil was dissolved in 25 c.c. of alcohol and saturated with moist carbon dioxide. After filtering from the precipitated benzamidine carbonate (2·5 grams) and evaporating in a vacuum, a mixture of oil and crystals was left (6·7 grams). The mixture was treated with 30 c.c. of water and 5 c.c. of concentrated aqueous ammonia, and heated in a reflux apparatus at 80°. The oil gradually disappeared, and after three hours the clear solution was evaporated to small bulk on the water-bath. After being kept in the cold, crystals of benzamide (1·46 grams) which separated were removed, and the filtrate was just neutralised with 10 per cent. hydrochloric acid. The last traces of benzamide were now removed by repeated extraction with ether, the aqueous solution was then treated with excess of 50 per cent. potassium hydroxide, and the oily base thus salted out was extracted twice with ethyl acetate. After removing the solvent in a vacuum, the crude base was left as a slightly discoloured oil (2·7 grams), which was purified by conversion into its normal oxalate by treatment with an alcoholic solution of anhydrous oxalic acid. The oxalate was obtained as a white, crystalline precipitate (2·0 grams), which was purified by recrystallisation from boiling methyl alcohol.

Isolation of the Free Base.—A concentrated aqueous solution of the oxalate was treated with 50 per cent. potassium hydroxide in excess, and the oil extracted by a large quantity of pure ether, in which it is not very soluble. The dried ethereal solution was freed from ether at 30° by means of a current of air, free from carbon dioxide and moisture. The base remained as a very pale yellow liquid, which on keeping crystallised in stout, colourless, transparent prisms, melting at 46°:

0·1885, by Kjeldahl's method, required 20·6 c.c. $N/10$-HCl. N = 15·3.

$C_{10}H_{14}ON_2$ requires N = 15·7 per cent.

Monobenzoyl-αγ-diaminopropane is very soluble in water or alcohol, readily so in chloroform or benzene, but only moderately so in ether (about 1 in 40). The following salts have been prepared:

The *Carbonate.*—An aqueous solution of the base absorbs carbon dioxide from the air, and on keeping leaves a crystalline carbonate. The same salt, which is readily soluble in water, but only moderately so in alcohol, was prepared from the base dissolved in alcohol by moist carbon dioxide:

0·2183 required 10·25 c.c. $N/10$-HCl. This corresponds with the formula $2C_{10}H_{14}ON_2,H_2CO_3$.

The *hydrochloride*, on evaporating its aqueous solution in a vacuum, remains as a syrup which crystallises (in tablets) only after a long time.

The *platinichloride* separates from fairly concentrated aqueous solutions as a yellow, microcrystalline precipitate; after recrystallisation from hot water it forms irregular, orange crystals, soluble in boiling alcohol, and melting and decomposing at 194°. For analysis it was dried at 100°:

0·1714 gave 0·0436 Pt. Pt = 25·44.

$(C_{10}H_{14}ON_2,HCl)_2PtCl_4$ requires Pt = 25·46 per cent.

The *picrate* separates from aqueous solutions of the base as a brownish-yellow, oily precipitate.

The *oxalate*, described above, crystallises in colourless needles, and melts and decomposes at 196°; it is readily soluble in water, but practically insoluble in alcohol:

0·1870, by Kjeldahl's method, required 17·0 c.c. $N/10$-HCl. N = 12·7.

$2C_{10}H_{14}ON_2,H_2C_2O_4$ requires N = 12·6 per cent.

The *hydrogen oxalate* was obtained by treating the normal salt with an excess of oxalic acid in aqueous solution, evaporating, and extracting with ether. It is a colourless, crystalline solid, readily soluble in alcohol (compare the normal salt). When the dilute alcoholic solution is precipitated by cautious addition of ether, a mass of needles is obtained, consisting of a mixture of normal and hydrogen oxalates of the base, owing to partial dissociation.

Hydrolysis of Monobenzoyl-αγ-diaminopropane.

By heating at 90° with 10 per cent. aqueous hydrochloric acid for seventy-five minutes the compound was completely hydrolysed, yielding benzoic acid and αγ-diaminopropane hydrochloride. By heating at 90° with 10 per cent. potassium hydroxide for two and a-quarter hours hydrolysis occurred to the extent of 90 per cent.

Benzoylation of Monobenzoyl-αγ-diaminopropane.

The base is very readily benzoylated by the Schotten-Baumann method, giving a practically quantitative yield of dibenzoyl-αγ-diaminopropane (m. p. 151°). (Found, N = 10·04. Calc., N = 9·93 per cent.)

A mixture of the substance with pure dibenzoyl-αγ-diaminopropane, obtained from αγ-diaminopropane, melted at 151°.

ORGANIC LABORATORY,
UNIVERSITY OF LIVERPOOL.

CCXLVIII.—*The Condensation of α-Keto-β-anilino-αβ-diphenylethane and its Homologues with Phenylcarbimide and with Phenylthiocarbimide.*

By SIDNEY ALBERT BRAZIER, M.Sc. (Priestley Research Scholar of the University of Birmingham) and HAMILTON McCOMBIE.

WHEN α-keto-β-anilino-αβ-diphenylethane (I) and phenylcarbimide are heated together, a compound results which has the formula $C_{27}H_{22}O_2N_2$, that is, direct addition of the two molecules has taken place:

$\mathrm{COPh{\cdot}CHPh{\cdot}NHPh}$ (I.)

$\mathrm{COPh{\cdot}CHPh{\cdot}NPh{\cdot}CO{\cdot}NHPh}$ (II.)

$\mathrm{HO{\cdot}CPh{:}CPh{\cdot}NHPh.}$ (III.)

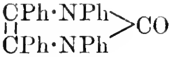
In α-keto-β-anilino-αβ-diphenylethane there are two possible points of attack for the phenylcarbimide. In the first place, the secondary amine grouping might be attacked, and the resulting compound would be desyl-*s*-diphenylcarbamide (II). That secondary amines do react with phenylcarbimide has been shown by Gebhardt in the case of diethylamine (*Ber.*, 1884, **17**, 3039) and methyl- and ethyl-aniline (*Ber.*, 1884, **17**, 2093).

In many reactions α-keto-β-anilino-αβ-diphenylethane and its derivatives are capable of reacting in the enolic form (III). Examples of this behaviour are furnished by its ready conversion into diphenylindole (Japp and Murray, *Ber.*, 1893, **26**, 2638; Lachewicz, *Monatsh.*, 1894, **15**, 402), by the conversion of the acyl derivatives into glyoxalines (Everest and McCombie, Trans., 1911, **99**, 1746), and the condensation with carbonyl chloride and thionyl chloride (McCombie and Parkes, this vol., p. 1991). If these reactions are taken into consideration, it is possible that phenylcarbimide might react with the hydroxyl group of the enolic form, resulting in the compound having the constitution IV.

On boiling the compound $C_{27}H_{22}O_2N_2$ with alcoholic hydrogen chloride, a molecule of water was eliminated, and a substance possessing the formula $C_{27}H_{20}ON_2$ was obtained. This substance was found to be very stable towards acids and alkalis, no salt with hydrochloric acid could be obtained (although a picrate could be prepared), and phosphorus pentachloride was without action on it. Starting with compounds represented by formulæ III and IV, water could be eliminated, resulting in compounds of formula V and VI respectively. The great stability of the compound argues against formula VI:

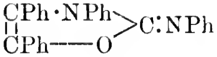
$\mathrm{CPh(NHPh){:}CPh{\cdot}O{\cdot}CO{\cdot}NHPh}$

(IV.)



$$\left.\begin{array}{l}\mathrm{CPh{\cdot}NPh}\\ \|\\ \mathrm{CPh{\cdot}NPh}\end{array}\right>\mathrm{CO}$$

(V.)



$$\left.\begin{array}{l}\mathrm{CPh{\cdot}NPh}\\ \|\\ \mathrm{CPh{-\!\!-}O}\end{array}\right>\mathrm{C{:}NPh}$$

(VI.)

A further argument against this formula is furnished by a study of the reaction between α-keto-β-anilino-αβ-diphenylethane and phenylthiocarbimide. In this case, after treating the reaction mixture with alcoholic hydrogen chloride, a compound free from oxygen, and having the formula $C_{27}H_{20}N_2S$ was obtained. The two possible formulæ for the intermediate product in this case are VII and VIII:

$\mathrm{CO{\cdot}Ph{\cdot}CHPh{\cdot}NPh{\cdot}CS{\cdot}NHPh}$ (VII.)

$\mathrm{CPh(NHPh){:}CPh{\cdot}O{\cdot}CS{\cdot}NHPh}$. (VIII.)

From a substance with the formula VIII, since the only oxygen atom is directly attached to the two carbon atoms, it would be impossible to eliminate the elements of water. From this it follows that the products formed by the action of phenyl-thiocarbimide and -carbimide respectively on α-keto-β-anilino-αβ-diphenylethane when treated with alcoholic hydrogen chloride are 1:3:4:5-*tetraphenyl*-2:3-*dihydro-2-glyoxalthione* * (IX) and 1:3:4:5-*tetraphenyl*-2:3-*dihydro-2-glyoxalone* (V):

$$\left.\begin{matrix}\text{CPh·NPh}\\ \|\\ \text{CPh·NPh}\end{matrix}\right>\text{CS}$$

(IX.)

The salts formed by the glyoxalones with picric acid gave some unexpected results. The picrates could be divided into two classes. Those derived from the tetraphenyl-, the triphenyl-*p*-tolyl-, and the triphenyl-β-naphthyl-glyoxalones were all red, and consisted of two molecules of the glyoxalone united with one molecule of picric acid. On the other hand, the picrates derived from the triphenyl-*m*-tolyl- and the triphenyl-*o*-tolyl-glyoxalones were yellow, and consisted of the glyoxalone and picric acid in equimolecular proportions.

EXPERIMENTAL.

The Action of Phenylcarbimide on α-Keto-β-anilino-αβ-diphenylethane.

Ten grams of α-keto-β-anilino-αβ-diphenylethane were heated on a water-bath with 4·6 grams of phenylcarbimide until a colourless, vitreous mass was formed. The excess of phenyl carbimide was removed by warming for a short time with a small quantity of methyl alcohol, and the white product, recrystallised from methyl alcohol, separated in white needles melting at 116—117°. It contained methyl alcohol of crystallisation. The yield was theoretical:

0·1963 gave 0·5558 CO_2 and 0·1049 H_2O. C = 77·22; H = 5·94.
0·2704 „ 15·3 c.c. N_2 at 12° and 747 mm. N = 6·57.
$C_{27}H_{22}O_2N_2,MeOH$ requires C = 76·70; H = 5·94; N = 6·39 per cent.

The product was sparingly soluble in cold alcohol, practically insoluble in cold benzene, but very soluble in hot benzene, from which it crystallised in needles melting at 124—125°, and contained benzene of crystallisation:

0·2017 gave 0·6013 CO_2 and 0·1090 H_2O. C = 81·30; H = 6·00.
$C_{27}H_{22}O_2N_2,C_6H_6$ requires C = 81·65; H = 5·78 per cent.

1:3:4:5-*Tetraphenyl*-2:3-*dihydro-2-glyoxalone*, $C_{27}H_{20}ON_2$.

The product obtained from the action of phenylcarbimide on α-keto-β-anilino-αβ-diphenylethane, when boiled for several hours

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* The termination "thione" appears to be a suitable one to designate a glyoxalone in which the CO-group is replaced by the CS-group.

with hydrochloric acid in alcohol, gave a substance which, after crystallisation from alcohol or benzene, separated in white needles melting at 204°. The compound is sparingly soluble in cold alcohol, more so in cold benzene, and very soluble in hot benzene or acetic acid:

0·2063 gave 0·6336 CO_2 and 0·0972 H_2O. C=83·76; H=5·24.
0·2154 „ 13·7 c.c. N_2 at 15° and 746·2 mm. N=7·27.
$C_{27}H_{20}ON_2$ requires C=83·50; H=5·16; N=7·22 per cent.

The glyoxalone is a very stable compound; its basicity is so slight that no hydrochloride could be prepared in either acetic acid or alcoholic solution. A picrate, however, was obtained. When the glyoxalone was heated in a sealed tube with aniline or phenylhydrazine, no condensation product could be isolated. Phosphorus pentachloride in benzene solution was without action on the glyoxalone.

The *picrate* was prepared by adding excess of picric acid to a concentrated solution of the glyoxalone in boiling acetic acid. The solution, on cooling, deposited dark red needles, which, after recrystallisation from absolute alcohol or acetic acid, melted at 171°:

0·1663 gave 0·4348 CO_2 and 0·0643 H_2O. C=71·30; H=4·30.
$2C_{27}H_{20}ON_2,C_6H_3O_7N_3$ requires C=71·65; H=4·29 per cent.

The picrate was readily decomposed by boiling with water or alkali, with regeneration of the glyoxalone. From the analysis it is evident that the salt contains two molecules of the base united with one molecule of picric acid.

3:4:5-*Triphenyl*-1-o-*tolyl*-2:3-*dihydro*-2-*glyoxalone*.

This compound, when crystallised from alcohol, melted at 193°:

0·1964 gave 0·6020 CO_2 and 0·0978 H_2O. C=83·6; H=5·52.
$C_{28}H_{22}ON_2$ requires C=83·57; H=5·47 per cent.

The *picrate* crystallises from acetic acid in yellow prisms melting at 169°:

0·2018 gave 0·4764 CO_2 and 0·0732 H_2O. C=64·40; H=4·02.
$C_{28}H_{22}ON_2,C_6H_3O_7N_3$ requires C=64·67; H=3·96 per cent.

Analysis shows that this salt consists of molecular proportions of the glyoxalone and picric acid.

3:4:5-*Triphenyl*-1-m-*tolyl*-2:3-*dihydro*-2-*glyoxalone*.

This compound crystallises from methyl alcohol or a mixture of benzene and light petroleum in slender needles melting at 185°:

0·1769 gave 0·5427 CO_2 and 0·0880 H_2O. C=83·67; H=5·53.
$C_{28}H_{22}ON_2$ requires C=83·57; H=5·47 per cent.

The *picrate* crystallises from absolute alcohol in yellow prisms melting at 172°:

0·2076 gave 0·4913 CO_2 and 0·0744 H_2O. C=64·6; H=3·98.

$C_{28}H_{22}ON_2,C_6H_3O_7N_3$ requires C=64·67; H=3·96 per cent.

Analysis shows that this salt consists of molecular proportions of the glyoxalone and picric acid.

3:4:5-*Triphenyl*-1-p-*tolyl*-2:3-*dihydro*-2-*glyoxalone.*

Five grams of α-keto-β-*p*-toluidino-αβ-diphenylethane were heated with 2 grams of phenylcarbimide on a water-bath for one and a-half hours. The product was then boiled for several hours with hydrogen chloride in alcoholic solution; the crystals were collected and recrystallised from absolute alcohol, when the substance separated in white needles melting at 206°. It is only sparingly soluble in cold solvents with the exception of acetic acid:

0·1941 gave 0·5943 CO_2 and 0·0965 H_2O. C=83·50; H=5·53.

$C_{28}H_{22}ON_2$ requires C=83·57; H=5·47 per cent.

The *picrate* crystallises from absolute alcohol in dark red needles melting at 188°:

0·1610 gave 0·4256 CO_2 and 0·0652 H_2O; C=72·1; H=4·5.

$2C_{28}H_{22}ON_2,C_6H_3O_7N_3$ requires C=72·04; H=4·55 per cent.

From the analysis it is seen that this picrate contains two molecules of the glyoxalone united with one molecule of picric acid.

3:4:5-*Triphenyl*-1-β-*naphthyl*-2:3-*dihydro*-2-*glyoxalone.*

This substance was prepared in the same way as the other compounds, and when recrystallised from methyl alcohol it gave masses of small, white needles, melting at 182—183°.

It is readily soluble in acetic acid, benzene, hot alcohol, or light petroleum, but less so in the cold solvents. It is sparingly soluble in ether, and is stable towards alkalis and acids:

0·1982 gave 0·6159 CO_2 and 0·0890 H_2O. C=84·76; H=4·99.

$C_{31}H_{22}ON_2$ requires C=84·91; H=5·02 per cent.

The *picrate* was obtained in acetic acid solution, and separated from absolute alcohol in pale red crystals melting at 201°:

0·2005 gave 0·5387 CO_2 and 0·0821 H_2O. C=73·30; H=4·55.

$2C_{31}H_{22}ON_2,C_6H_3O_7N_3$ requires C=73·85; H=4·25 per cent.

Analysis shows that the glyoxalone and picric acid are present in the proportion of 2:1

Preparation of 1:3:4:5-*Tetraphenyl*-2:3-*dihydro*-2-*glyoxalthione and its Homologues.*

These compounds were prepared in a manner similar to that employed in the preparation of the corresponding glyoxalones. The anilino-derivative and the phenylthiocarbimide were heated together for a few hours in an air-bath, or for a longer time on a water-bath. Water was then eliminated from the compound by boiling with alcoholic hydrogen chloride.

The glyoxalthiones thus prepared are only sparingly soluble in methyl or ethyl alcohols, more readily so in amyl alcohol or acetic acid, and very soluble in acetone or benzene.

1:3:4:5-*Tetraphenyl*-2:3-*dihydro*-2-*glyoxalthione*, $C_{27}H_{20}N_2S$.

This substance crystallises from glacial acetic acid in slender, white needles, melting at 249—250°:

0·2068 gave 0·6059 CO_2 and 0·0936 H_2O. C=79·90; H=5·03.
0·2002 „ 11·95 c.c. N_2 at 14·2° and 752·8 mm. N=6·91.
0·3716 „ 0·2166 $BaSO_4$. S=8·01.
$C_{27}H_{20}N_2S$ requires C=80·19; H=4·96; N=6·93; S=7·92 per cent.

3:4:5-*Triphenyl*-1-o-*tolyl*-2:3-*dihydro*-2-*glyoxalthione.*

When recrystallised from amyl alcohol this compound melted at 240°:

0·2046 gave 0·6018 CO_2 and 0·0952 H_2O. C=80·22; H=5·17.
$C_{28}H_{22}N_2S$ requires C=80·38; H=5·26 per cent.

3:4:5-*Triphenyl*-1-m-*tolyl*-2:3-*dihydro*-2-*glyoxalthione.*

When recrystallised from absolute alcohol this substance separated in slender, white needles, melting at 189°:

0·1987 gave 0·5851 CO_2 and 0·0963 H_2O. C=80·30; H=5·39.
$C_{28}H_{22}N_2S$ requires C=80·38; H=5·26 per cent.

3:4:5-*Triphenyl*-1-p-*tolyl*-2:3-*dihydro*-2-*glyoxalthione.*

This substance was obtained in slender needles melting at 234°, after recrystallisation from glacial acetic acid or amyl alcohol:

0·2041 gave 0·6004 CO_2 and 0·0992 H_2O. C=80·24; H=5·40.
$C_{28}H_{22}N_2S$ requires C=80·38; H=5·26 per cent.

α-Keto-β-2-naphthylamino-αβ-diphenylethane, $\mathrm{COPh{\cdot}CHPh{\cdot}NH{\cdot}C_{10}H_7}$.

This compound has been prepared by Bischla and Fireman (*Ber.*, 1893, **26**, 1339) by the decomposition of β-bromo-α-keto-αβ-diphenylethane with β-naphthylamine in alcoholic solution, and also by Voigt (*J. pr. Chem.*, 1886, [ii], **34**, 22) from benzil and β-naphthylamine at 215°.

We have prepared it from benzoin in the usual manner, by heating the two substances together in an air-bath at 150° for three and a-half hours. The product was crystallised from amyl alcohol, when it melted at 131—132°.

The hydrochloride was obtained in slender crystals, melting and decomposing at 200°.

3 : 4 : 5-*Triphenyl*-1-β-*naphthyl*-2 : 3-*dihydro*-2-*glyoxalthione.*

This compound was more difficult to prepare owing to charring taking place. After repeated recrystallisations from amyl alcohol, crystals melting at 219° were obtained. This glyoxalthione is readily soluble in acetone or benzene, and sparingly so in cold methyl or ethyl alcohols:

0·2015 gave 0·6035 CO_2 and 0·0910 H_2O. C = 81·70; H = 5·01.

$C_{31}H_{22}N_2S$ requires C = 81·91; H = 4·85 per cent.

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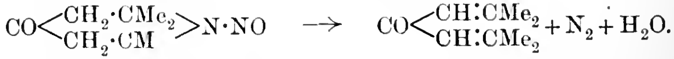
CCXLIX.—*The Catalytic Decomposition of Nitrosotriacetonamine by Alkalis.*

By Douglas Arthur Clibbens and Francis Francis.

The formation of phorone by the decomposition of nitrosotriacetonamine was observed by Heintz (*Annalen*, 1877, **187**, 250), and may be expressed as follows:



$$\mathrm{CO}{<}\begin{matrix}\mathrm{CH_2{\cdot}CMe_2}\\ \mathrm{CH_2{\cdot}CM}\end{matrix}{>}\mathrm{N{\cdot}NO} \longrightarrow \mathrm{CO}{<}\begin{matrix}\mathrm{CH{:}CMe_2}\\ \mathrm{CH{:}CMe_2}\end{matrix} + \mathrm{N_2} + \mathrm{H_2O}.$$

The method he described for the preparation consisted in heating the nitrosoamine with a concentrated aqueous solution of sodium hydroxide, nitrogen was evolved, and the reaction completed by boiling for four hours under a reflux condenser. Phorone was extracted from the reaction mixture by means of ether, and purified by fractional distillation, but the yield obtained was not stated. The preparation of triacetonamine has been investigated in this laboratory, and an easy and inexpensive method for its production in quantity has been found, an account of which will form the subject of a further communication.

In the course of a re-investigation of this base (*Ber.*, 1912, **45**, 2060) the decomposition of its nitrosoamine was studied. It was found that the yield of phorone obtained by following Heintz's method was small, and further that it was accompanied by at least one other product. If the reaction, however, is carried out in alcoholic solution and a trace of alkali only is used, the decomposition of the nitrosoamine into nitrogen, water, and phorone takes place smoothly at low temperatures, and a nearly quantitative yield of the unsaturated ketone is obtained. The reaction also takes place in ethereal or aqueous solution, and the decomposition of the nitrosoamine appears to be due to the catalytic influence of the base, since it follows the same course with the hydroxides of potassium, sodium, barium, calcium, or ammonium.

The conversion of triacetonamine into its nitroso-derivative is carried out in the usual manner, and the latter substance is purified by crystallisation from dilute alcohol or from a mixture of benzene and light petroleum; in the solid state it appears to be perfectly stable, and an alcoholic solution may be preserved for a considerable period in the dark without undergoing decomposition.

The nitrosoamine is extremely soluble in alcohol, ether, or benzene, whereas in water it is only soluble to the extent of about 6·5 grams per litre at the ordinary temperature, but this solution is unstable, becoming slightly acid after a few days.

For the preparation of phorone, the pure recrystallised nitrosoamine is dissolved in an equal weight of alcohol, and warmed on a water-bath with 1 or 2 c.c. of a very dilute solution of potassium ethoxide; a brisk effervescence due to the evolution of nitrogen sets in, and the temperature should not be allowed to rise above 40°; within half-an-hour the reaction is complete. Between 50 and 60 per cent. of the possible amount of phorone may be obtained in a high state of purity by cooling the solution in a freezing mixture, when it crystallises out and must be rapidly collected; a further amount, in all, about 90—95 per cent., can be obtained by evaporating the filtrate and further cooling. A more convenient process when dealing with large quantities, but one which does not give a dry product, consists in pouring the alcoholic solution into brine, separating off the phorone layer, and allowing it to crystallise.

Whatever method is adopted for isolating the product, however, it is always accompanied by a small quantity of a liquid, which, although largely consisting of phorone, appears to contain another substance, the accumulation of which prevents the phorone from crystallising out, even at very low temperatures.

Rate of Catalysis by Hydroxyl Ions.

This interesting decomposition appeared to us to be worth following quantitatively, because the preliminary work had clearly indicated the probability that we might be dealing with a decomposition which would afford a means for the quantitative determination of hydroxyl ions, for which at present there exists no method comparable to that of the diazoacetic ester one for the hydrogen ion (Bredig and Fraenkel). The present paper deals with the first part of our investigation, and only describes the experiments carried out with sodium hydroxide, but we consider that they render it very probable that our expectations may be realised.*

Method Employed.

The decomposition of the nitrosoamine was easily followed by measuring the rate of evolution of nitrogen, and for this purpose an apparatus was used similar to that employed by J. H. Walton in studying the catalysis of hydrogen peroxide by iodine (*Zeitsch. physikal. Chem.*, 1904, **47**, 185) with the modifications in the mode of shaking described by McBain (*Diss.*, Heidelburg, 1908). The reaction was generally carried out in a Jena-glass flask, but in the experiments with very dilute alkali a silver flask and dropping tube were employed. At the commencement of the investigation we considerably under-estimated the solubility of the nitrosoamine in water, and consequently the first experiments were carried out in aqueous alcohol solution. In these a suitable volume of an alcoholic solution of the nitrosoamine was measured into the reaction flask, together with sufficient water or alcohol to make a solution of the required proportions. The aqueous solution of the alkali was contained in the small dropping tube. Occasionally this arrangement was reversed, that is, the solution of alkali, diluted with alcohol when required, was placed in the reaction flask, and the solution of the nitrosoamine into the dropping tube. But in the later experiments, carried out in aqueous solutions, a different course was adopted. About 0·13 gram of the nitrosoamine was

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* The water used in the various determinations was the ordinary laboratory distilled water, freed from carbon dioxide by the passage of air free from carbon dioxide; the alcohol employed was the absolute alcohol of commerce, and the sodium hydroxide, free from carbonate, was prepared from sodium by the usual method.

weighed into the flask, which was then set up and shaken in the thermostat at 30° with the desired volume of water until complete solution had taken place; the dropping tube containing the alkali was then inserted, and, after thermal equilibrium had been attained, this was released, and readings of the evolved nitrogen were commenced.

At lower temperatures, when the velocity of the reaction was not too large, the solution of alkali was allowed to run direct into the reaction flask through the side-tube, and readings commenced only after the mixture had attained the temperature of the bath. In order to avoid initial irregularities, apparently due to effects of saturation and supersaturation, the zero reading was taken after about 1 c.c. of nitrogen had been collected; no corrections for temperature or pressure were necessary, except in those experiments where the actual end reading had to be taken after the lapse of a considerable period.

In the apparatus a quantitative estimation of the amount of nitrogen evolved from the nitrosoamine gave us data within 2·5 per cent. of the calculated amount, both when dilute and concentrated solutions of sodium hydroxide were employed.

Order of the Reaction.

It was expected that if the decomposition of nitrosotriacetonamine was correctly expressed by the equation given at the commencement of this paper, it would proceed according to the first order equation:

$$k = \frac{2{\cdot}303}{t}\log\frac{a}{a-x},$$

where a is the amount of nitrosoamine present, and is proportional to the total volume of nitrogen evolved; x is the amount present after the time t (minutes) has elapsed, and is proportional to the volume of nitrogen evolved during the time t. For convenience the equation may be written:

$$k = \frac{2{\cdot}303}{t}\log\frac{V_\infty - V_0}{V_\infty - V}.$$

V_0 is the burette reading at the time taken as zero, V is the reading at time t, and V_∞ is the infinity reading. For V_0 a reading was chosen near the commencement of the reaction, when the initial irregularities, observed in each experiment, had ceased.

Throughout the following series of experiments, except where otherwise indicated, the concentration of the nitrosoamine is given in mols. per litre, that of the sodium hydroxide in normality; and the composition of the solvent is expressed in per cent. by volume.

SERIES A.

Sodium Hydroxide in Small Concentration.

A large number of experiments has shown that the unimolecular formula in all cases gives a constant within the limits of experimental error—about 3 per cent.—when the catalyst is sodium hydroxide in small concentrations; from 0·03*N* downwards in the case of aqueous alcohol, or from 0·05*N* downwards when water alone was used as solvent.

From the many experiments carried out, four are given in table I, which suffice to show the degree of agreement obtained.

TABLE I.

Expt. 43.—75 per cent. Water, 25 per cent. Alcohol.

$t = 30·0°$; catalyst 0·002*N*-NaOH.

t (minutes).	*V* (c.c.).	*k*.
0	4·51	—
12	5·17	0·00217
20	5·58	0 00212
28	5·98	0·00210
44	6·80	0·00212
68	7·87	0·00206
92	8·98	0·00208
116	10 04	0·00209
∞	30·2	—
	Mean	0·00210

Expt. 5.—50 per cent. Water, 50 per cent. Alcohol.

$t = 29·84°$; catalyst 0·005*N*-NaOH.

t (minutes).	*V* (c.c.).	*k*.
0	4·29	—
4	5·17	0·00967
10	6·35	0·00931
16	7·41	0 00904
22	8·49	0·00908
28	9·38	0·00904
36	10·63	0·00887
44	11·81	0·00890
52	12·88	0·00889
60	13·93	0·00895
68	14·83	0·00890
76	15·71	0 00891
84	16·50	0·00889
92	17·30	0·00894
∞	27 5	—
	Mean	0 00894

Expt. 58.—100 per cent. Water.

$t = 30·0°$; catalyst 0·01*N*-NaOH.

0	4·98	—
8	7·42	0·0170
14	9·10	0·0173
22	11·10	0·0175
26	12·01	0·0176
34	13·55	0·0175
44	15·30	0·0176
60	17·40	0·0175
∞	24·1	—
	Mean	0·0174

Expt. 16.—50 per cent. Water, 50 per cent. Alcohol.

$t = 29·99°$; catalyst 0·02*N*-NaOH.

0	2·45	—
4	4·90	0·0289
8	7·00	0·0283
12	8·98	0·0287
16	10·80	0·0291
20	12·22	0·0285
24	13·71	0·0290
28	14·92	0·0290
32	15·94	0·0287
36	16·98	0·0290
40	17·88	0·0291
∞	24·9	—
	Mean	0·0288

The results are given in full since it is necessary to note the presence or absence of "drift" in the constants when considering the possibility of using a reaction of this kind as a general method for the determination of "hydroxyl" concentration.

Table I*a* gives a summary of the work carried out in pure water with small concentrations of alkalis. Several duplicate experiments are included in order to show the degree of reproducibility of the results.

Table I*b* contains experiments carried out in solutions containing alcohol.

TABLE I*a*.

Solvent, 100 per cent. Water.

	Concentration of			Constant.		
Expt. No.	Nitroso-amine.	NaOH.	*t*°.	*k* minimum—	*k* maximum.	Mean.
56	0·18	0·005*N*	30·0°	0·00848	0·00892	0·00871
94	0·32	0·006*N*	30·0	0·00973	0·00999	0·00985
59	0·24	0·0067*N*	30·0	0·0106	0·0108	0·0107
95	0·31	0·0095*N*	30·0	0·0150	0·0155	0·0152
58	0·18	0·01*N*	30·0	0·0170	0·0176	0·0174
92	0·29	0·0121*N*	30·1	0·0209	0·0218	0·0212
105	0·29	0·0121*N*	30·2	0·0210	0·0217	0·0213
106	0·29	0·0121*N*	30·0	0·0206	0·0210	0·0209
93	0·28	0·0145*N*	30·1	0·0255	0·0265	0·0260
107	0·28	0·0145*N*	30·0	0·0266	0·0270	0·0268
102	0·28	0·0145*N*	30·2	0·0262	0·0268	0·0264
99	0·27	0·0167*N*	30·0	0·0280	0·0299	0·0289
61	0·28	0·02*N*	30·0	0·0353	0·0378	0·0364
60	0·27	0·023*N*	30·0	0·0405	0·0429	0·0414
85	0·28	0·03*N*	30·0	0·0447	0·0575	0·0513
86	0·28	0·04*N*	30·1	0·0679	0·0688	0·0683
88	0·32	0·0454*N*	30·1	0·0769	0·0782	0·0773
87	0·28	0·05*N*	30·1	0·0871	0·0884	0·0876

TABLE I*b*.

	Concentration of				Constant.		
Expt. No.	Nitroso-amine.	NaOH.	Per cent. alcohol.	*t*°.	*k* minimum—	*k* maximum.	Mean.
43	0·125	0·002*N*	25	30·0°	0·00206	0·00217	0·00210
39	0·125	0·005*N*	25	30·0	0·00872	0·00908	0·00892
38	0·125	0·005*N*	25	30·0	0·00887	0·00895	0·00894
30	0·05	0·01*N*	25	30·0	0·0153	0·0157	0·0156
5	0·05	0·005*N*	50	29·84	0·00887	0·00967	0·00894
6	0·05	0·007*N*	50	29·84	0·00960	0·0106	0·00967
3	0·05	0·01*N*	50	29·92	0·0165	0·0168	0·0166
16	0·05	0·02*N*	50	29·99	0·0283	0·0291	0·0288
14	0·05	0·03*N*	50	30·0	0·0405	0·0439	0·0437
40	0·125	0·005*N*	75	29·8	0·0113	0·0119	0·0116
33	0·05	0·01*N*	75	30·0	0·0152	0·0159	0·0155
42	0·125	0·002*N*	90	30·0	0·00474	0·00483	0·00478
41	0·125	0·005*N*	90	30·0	0·0136	0·0143	0·0138

In a reaction of the first order, the velocity of the reaction is independent of the initial concentration of the reagent, and, within experimental error, this has been shown to be the case in the decomposition of nitrosotriacetonamine. In table II two reactions are compared; in the second the initial concentration of the nitrosoamine is double that in the first; otherwise the conditions are similar, and the constant is the same within 3·3 per cent. in both cases.

TABLE II.

Solvent: 50 per cent. Alcohol, 50 per cent. Water.

Concentration of Catalyst, 0·02N-NaOH.

			Constant.		
Expt. No.	Concentration of nitrosoamine in 100 c.c. of reaction mixture.	$t°$.	k minimum—	k maximum.	Mean.
16	0·0953 gram	29·99	0·0283	0·0291	0·0288
21	0·1906 ,,	29·98	0 0272	0·0280	0·0279

SERIES B.

Sodium Hydroxide in High Concentrations.

In all experiments, irrespective of the concentration of the catalyst and of the nature of the solvent, irregularities are observed at the commencement of the reaction. The first-order constants obtained from the initial readings generally increase steadily, reaching a constant value after the evolution of 2 or 3 c.c. of nitrogen. When, however, the concentration of the sodium hydroxide approaches 0·03 to 0·04N, the constants commence to "drift," until, the change being quite continuous, all constancy in the first-order constants finally disappears.

However, on still further increasing the concentration of the alkali, a similar series of changes is observed in the reverse order, until, with 0·5N and higher alkali concentration, an excellent first-order constant is again obtained over the whole range of the reaction.

Consequently, there are two concentration limits, an upper and a lower, varying somewhat with the nature of the solvent employed, and approximately 0·3N- and 0·03N-sodium hydroxide in the case of aqueous alcohol—between which the first-order equation does not hold, but for all other concentrations examined the expression

$$\frac{2{\cdot}303}{t}\log\frac{V_\infty - V_0}{V_\infty - V}$$

remains constant within experimental error. The type of "drift" observed in two experiments is shown in detail in table III. The next two tables, III*a* and III*b*, are continuations of I*a* and I*b*, and summarise experiments carried out with higher concentrations of sodium hydroxide in water and aqueous alcohol respectively.

Table III.

Expt. 12.—50 per cent. Water, 50 per cent. Alcohol.

$t = 29·8°$; catalyst 0·04*N*-NaOH.

t (minutes).	*V* (c.c.).	*k*.
0	3·82	—
4	7·90	0·0533
8	11·41	0·0552
12	14·32	0·0567
16	16·70	0·0581
20	18·60	0·0593
24	20·10	0·0604
28	21·27	0·0613
32	22·24	0·0620
36	22·93	0·0634
∞	25·1	—

Expt. 11.—50 per cent. Water, 50 per cent. Alcohol.

$t = 29·8°$; catalyst 0·1*N*-NaOH.

t (minutes).	*V* (c.c.).	*k*.
0	4·78	—
2	7·31	0·0669
4	9·91	0·0732
6	12·32	0·0778
10	16·30	0·0844
12	17·87	0·0869
14	19·22	0·0895
16	20·34	0·0918
18	21·21	0·0930
20	22·10	0·0971
∞	25·0	—

Table III*a*.

Solvent, 100 per cent. Water.

Expt. No.	Concentration of		*t*°.	Constant.		
	Nitroso-amine.	NaOH.		*k* minimum—	*k* maximum.	Mean
64	0·21	0·04*N*	14·3°	0·0147	0·0152	0·0148
65	0·18	0·05*N*	14·3	0·0170	0·0180	0·0175
74	0·28	0·08*N*	14·6	0·0234	0·0264	—
66	0·28	0·1*N*	15·4	0·0274	0·0308	—
72	0·28	0·1*N*	14·7	0·0260	0·0325	—
73	0·28	0·2*N*	14·7	0·0252	0·0314	—
76	0·14	0·3*N*	14·5	0·0255	0·0277	0·0262
77	0·21	0·4*N*	14·5	0·0193	0·0198	0·0196
75	0·18	0·5*N*	14·6	0·0136	0·0140	0·0138

Table III*b*.

Expt. No.	Concentration of		Per cent. alcohol.	*t*°.	Constant.		
	Nitroso-amine.	NaOH.			*k* minimum—	*k* maximum.	Mean.
26	0·05	0·03*N*	25	30·01°	0·0535	0·0565	0·0554
36	0·05	0·05*N*	25	30·0	0·0742	0·0753	0·0745
35	0·05	0·3*N*	25	29·9	0·0972	0·1042	0·1017
25	0·05	0·5*N*	25	30·02	0·0662	0·0749	0·0726
31	0·05	0·7*N*	25	30·0	0·0426	0·0434	0·0430
29	0·05	1·0*N*	25	29·82	0·0260	0·0267	0·0266
28	0·05	2·0*N*	25	29·82	0·00942	0·0106	0·0101
14	0·05	0·03*N*	50	30·00	0·0421	0·0439	0·0437
12	0·05	0·04*N*	50	29·8	0·0533	0·0634	—
7	0·05	0·05*N*	50	29·9	0·0593	0·0713	—
11	0·05	0·1*N*	50	29·8	0·0669	0·0971	—
20	0·10	0·2*N*	50	29·93	0·0572	0·0654	—
13	0·05	0·3*N*	50	30·0	0·0423	0·0437	0·0430
9	0·05	0·5*N*	50	29·90	0·0244	0·0248	0·0246
22	0·10	0·5*N*	50	29·98	0·0241	0·0250	0·0246
18	0·05	1·0*N*	50	29·8	0·00846	0·00907	0·00887
17	0·05	2·0*N*	50	29·8	0·00733	0·00753	0·00741
34	0·05	0·5*N*	75	29·98	0·0121	0·0129	0·0123

The range of concentrations, over which the "drift" in the constants occur, is slightly displaced towards the region of high concentrations by an increase in the proportion of water in the solvent; for example, a regular "drift" in the constants, over the whole range of the reaction, is first observed with 0·04N-sodium hydroxide in 50 per cent. aqueous-alcoholic solution.

In pure aqueous solution this concentration of alkali yields good constants, and even with 0·05N-alkali the "drift" is only observed near the beginning of the reaction; variations in temperature do not appreciably alter the "drift" range.

Relation between Concentration of Alkali and Rate of Reaction.—I.

A study of the variation in the rate of the reaction with the concentration of the catalyst has thus led to results of peculiar and somewhat unexpected interest. It will be seen from tables I*b* and III*b*, where the solvent was 50 per cent. alcohol and water, that, commencing with a concentration of 0·003N-sodium hydroxide, the effect of increasing the concentration results in a regular increase in the rate of reaction, which reaches a maximum in the neighbourhood of 0·03—0·2N-alkali. The mean value for k rises from 0·00357 with a concentration of alkali of 0·003N to 0·0437 when it has increased to 0·03N, and the value increases over the "drift" range up to 0·2N, when the average value to k is 0·0650.

Further increase in the alkali concentration results in a regular decrease in the rate of reaction, namely, from $k=0·0430$ with a concentration of 0·3N down to 0·00887 in the case of 1·0N.

Since the rate of reaction cannot be accurately compared in the medium alkali concentrations by means of the first-order constants, there is appended in table IV the time takesn to collect 10 c.c. of nitrogen in a few experiments. The amount of nitrosoamine used in each was about 0·05M, and therefore the periods should be inversely proportional to the velocity-constant; they serve as a comparative measure of the rate of reaction.

TABLE IV.

Expt. No.	Concentration of NaOH.	k mean.	$t°$.	Time (in minutes) to collect 10 c.c. N_2.
10	0·003N	0·00357	29·9°	159
6	0·007N	0·00970	29·84	56
3	0·01N	0·0166	29·92	34
16	0·02N	0·0288	29·99	19
14	0·03N	0·0437	30·0	13·5
12	0·04N	—	29·8	11
7	0·05N	—	29·9	11
11	0·1N	—	29·80	9
13	0·3N	0·0435	30·0	13
9	0·5N	0·0246	29·9	22
18	1·0N	0·00887	29·8	60

It will be seen that the reaction proceeds faster in the presence of 0·007*N*-alkali than in the presence of *N*-alkali. The reaction, however, still proceeds to the end, even in the most alkaline solutions, that is, all the nitrogen is evolved. It will be observed that the concentrations in which the rate of reaction reaches a maximum are just those for which the first-order equation breaks down.

A similar behaviour in the variations in the rate of reaction with the alkali concentration is also observed when solvents containing proportions of alcohol other than 50 per cent. are employed, and a careful study of this rate has been made on the dilute side of the maximum using pure water. The results summarised from table I*a* are given in table V, which contains in the third column the hydroxyl ion concentration corresponding with that of the alkali employed. The values given have been interpolated from the measurements of A. A. Noyes on the conductivity of aqueous solutions of sodium hydroxide ("The Electrical Conductivity of Aqueous Solutions," *Carnegie Institution of Washington*, Publication No. 63, 1907, p. 268).

TABLE V.

	Concentration of				
Expt. No.	NaOH.	$\overline{\mathrm{OH}}$.	*k* mean.	*k*/NaOH.	*k*/OH′.
56	0·005*N*	0·0049*N*	0·00871	1·74	1·78
59	0·0067*N*	0·0065*N*	0·0107	1·60	1·65
58	0·01*N*	0·0096*N*	0·0174	1·74	1·81
61	0·02*N*	0·0190*N*	0·0364	1·82	1·91
60	0·023*N*	0·0218*N*	0·0414	1·80	1·89
85	0·03*N*	0·0282*N*	0·0513	1·71	1·82
86	0·04*N*	0·0374*N*	0·0683	1·71	1·82
88	0·045*N*	0·0422*N*	0·0773	1·71	1·83
87	0·05*N*	0·0463*N*	0·0876	1·75	1·89

It is seen that the first-order constant is approximately proportional to the concentration of the alkali, but when compared with that of the hydroxyl ion the proportionality holds within the limits of the experimental error.

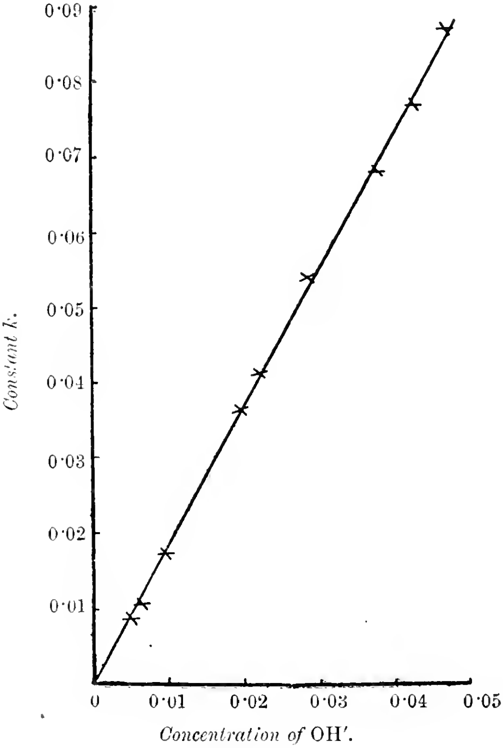
This may also be seen from Fig. 1, in which the constant has been plotted vertically against the concentration of the hydroxyl ions horizontally.

Relation between Concentration of Alkali and Rate of Reaction in Aqueous Solution.—II.

In pure aqueous solutions at still higher concentrations of alkali than those just discussed, that is, within the "drift" region, the reaction proceeds too rapidly at 30° for accurate measurement, and in consequence such experiments were carried out at 14·5°. These are recorded in the previous table, III*a*. The proportionality between concentration of alkali and constant holds until the "drift" commences.

We refrain from giving detailed data of such constants, since the nature of the "drift" may be appreciated from the statement that for 0·1*N* concentration of sodium hydroxide in aqueous solution the constant rises steadily from 0·0260 to 0·0325, and in the case of 0·2*N*-alkali from 0·0252 up to 0·0314.

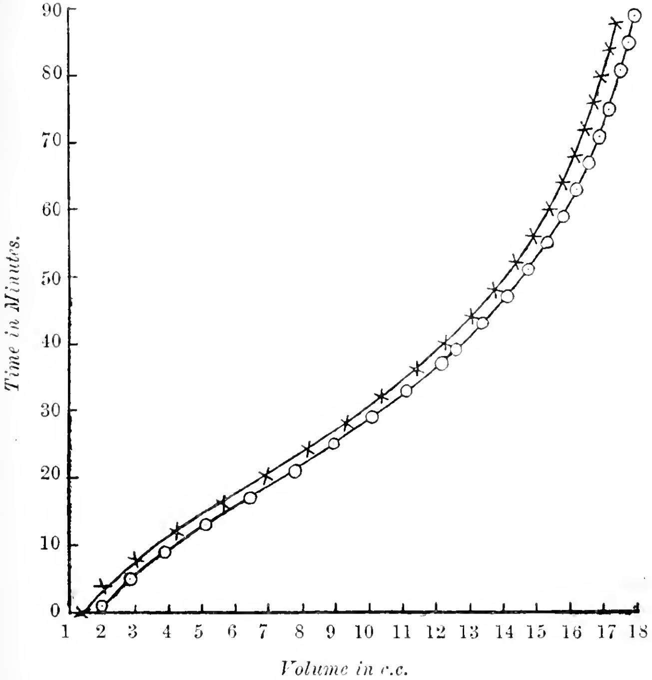
FIG. 1.



In spite of the difference between the concentrations of the alkali, these two reactions are almost identical throughout, as may be seen in Fig. 2, where the volume of nitrogen evolved has been plotted against the time.

In the immediate neighbourhood of the maximum rate, where the "drift" in the constants is most marked, a variation in the concentration of the alkali produces a comparatively slight change in the constants, indicated in table VI, where the constant k in the column headed "average" indicates that the first-order constants are drifting, and the average value has been recorded.

FIG. 2.



The rates for the concentrations of alkali above and below the region of "drift" yield fairly good constants.

TABLE VI.

Expt. No.	Concentration of NaOH.	k mean value.	k average.
64	0·04N	0·0148	—
65	0·05N	0 0175	—
74	0·08N	—	0·0252
72	0·1N	—	0·0291
73	0·2N	—	0·0287
76	0·3N	—	0·0262
77	0·4N	0·0196	—
75	0·5N	0·0138	—

Relation between Rate of Reaction and Nature of Solvent.

A series of experiments carried out in aqueous solutions containing varying amounts of alcohol show that the effect of the latter substance on the concentrated side of the maximum (table III*b*) is much greater in retarding the reaction than the effect it produces on the dilute side (table I*b*). This influence is parallel to the effect of alcohol on the dissociation of sodium hydroxide, and hence on the concentration of hydroxyl ions. The effect of 50 and 25 per cent. of alcohol on the mean value of k for different concentrations of alkali is illustrated in table VII.

TABLE VII.

Expt. No.	Concentration of NaOH.	$t°$.	k 50 per cent. alcohol.	k 25 per cent. alcohol.	$t°$.	Expt. No.
5	0·005N	29·84	0·00894	0·00892	30·0	39
3	0·01N	29·92	0·0166	0·0156	30·0	30
14	0·03N	30·0	0·0437	0·0554	30·01	26
13	0·3N	30·0	0·0430	0·1017	29·9	35
9	0·5N	29·90	0·0246	0·0726	30·02	25
18	1·0N	29·8	0·00887	0·0266	29·82	29

Temperature-coefficient.

This coefficient determined from experiment No. 64, and taking the mean value for k from 62 and 86, gives a value of 3·18. Also from experiments 65 and 87 the value 3·17 is obtained, but it will be noticed that the experiments which lend themselves to this determination happen to lie in the region where variations in the alkali-concentration have least effect on the constant, and in consequence of this no great stress can be laid on these values.

Mechanism of Reaction.

In view of the uncertainty which is always attached to any explanation of the mechanism of a reaction arrived at solely from kinetic measurements, it is only possible to advance a very tentative view as a feasible explanation of the peculiar quantitative results described in this preliminary communication. If the formation of an isomeric form of the nitrosoamine be postulated, and if it be further supposed that such a form is incapable of being decomposed into phorone and nitrogen under the influence of hydroxyl ions, a partial explanation at least can then be offered for the results we have obtained. Without laying any stress on the nature of the intermediate substance and provisionally calling it the α-nitrosoamine, it may be supposed that the hydroxyl ion has two effects: first, that it can positively catalyse the reaction nitrosoamine $\longrightarrow$ nitrogen + phorone, and secondly, it displaces to the right the instantaneous equilibrium nitrosoamine $\rightleftharpoons$ α-nitrosoamine. The first reaction is that always measured, and its velocity increases with the hydroxyl-concentration, but as this concentration approaches and reaches excess, more and more of the nitrosoamine is held in the form of the non-reactive α-isomeride, until in concentrated solutions of alkali, although the reaction is intrinsically quicker, the total effect is an actual decrease in the velocity of the reaction, since less and less of the nitrosoamine is available, at any given moment, in the reactive form.

Clearly other alternative hypotheses could be advanced, but we expect to obtain further light on the course of the reaction during the more complete investigation of the decomposition which is now being carried out. The effects of neutral salts and the data for barium hydroxide will be published shortly.

The preliminary work described in this communication strengthens our belief in the value of the decomposition as a means for the determination of hydroxyl concentrations, in aqueous and aqueous-alcoholic solutions, up to 0·05*N* and beyond 0·3*N*.

Our thanks are due to Dr. James W. McBain for the help he has afforded us during the progress of the investigation.

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CCL.—*Photo-kinetics of Sodium Hypochlorite Solutions.*

By William Cudmore McCullagh Lewis.

The photochemical decomposition of aqueous hypochlorite solutions is from the technical side a subject of considerable importance, and the present work was begun with the idea of examining the velocity with which such photochemical efforts take place. To reduce secondary effects to a minimum it is neessary to study a homogeneous system, and hence the choice of the sodium salt.

The decomposition of sodium hypochlorite solutions by heat has been fairly fully investigated by Bhaduri (*Zeitsch. anorg. Chem.*, 1897, **13**, 385) at 25° and 100°. At the lower temperature there is a slight formation of sodium chlorate, the main reaction being, however, $2NaClO \longrightarrow 2NaCl + O_2$. The degree of decomposition (in the dark) was small. At the higher temperature the extent of the reaction is much greater, both sodium chlorate and free oxygen being produced, the ratio of the chlorate oxygen to free oxygen varying from 1:0·306 to 1:6·39 according to initial concentration and time of heating. At this temperature Bhaduri assumes the applicability of the equation $3NaClO \longrightarrow NaClO_3+2NaCl$ as representing the main direction of decomposition, although one may show on his own data that a termolecular velocity equation does not give a constant. This may be due, however, to the fact that Bhaduri's method of working with sealed tubes is perhaps unsuitable for such calculation. An important point brought out by Bhaduri is that at 100° the percentage decomposition of the hypochlorite (after a given time) passes through a minimum at a point corresponding with the initial sodium hypochlorite concentration 1·5 to 1·7 per cent.

To avoid the complications which evidently enter at the higher temperature, the decomposition of the hypochlorite, described in this paper, was carried out in the region of 25°.

EXPERIMENTAL.

The source of light employed was an immersion type of Shott's mercury uviol lamp. The current could be varied between 3 and 5 amperes when necessary, steady burning being attained by the introduction of a self inductance into the circuit. The lamp was placed vertically in a cylinder containing the solution, the lamp being protected by a sheath of uviol glass. With an arrangement such as this one obtains the maximum effect of which the lamp is capable. The solution was kept in the neighbourhood of 25° by means of a stream of water through a glass spiral. Stirring was effected by a stream of air bubbles.

A preliminary experiment was carried out with distilled water. The current being 3·5 amperes, the exposure lasted for seven hours, but no trace of hydrogen peroxide could be detected by means of titanous sulphate. The effects observed in the hypochlorite solutions are therefore not due to secondary reactions with a partly decomposed solvent.

Analysis of the Hypochlorite Solution Before and After Exposure.—The solution employed was the usual commercial material containing some sodium chloride and sodium hydroxide. The amount of hypochlorite was determined by titration with arsenious oxide and starch-iodide paper. The quantity of chloride was determined by the Volhard method after addition of known excess of arsenious oxide and decomposition of the arsenate by dilute nitric acid. By dilution with distilled water the solutions examined were made approximately decinormal with respect to hypochlorite.

In the first experiment, with a current of 4·25 amperes the length of exposure was four hours fifteen minutes. In a second experiment the exposure lasted five hours, the current being 3·5 amperes. If the reaction is represented by the expression $NaClO \longrightarrow NaCl + O$, or $2NaClO \longrightarrow 2NaCl + O_2$, one equivalent of sodium chloride should be produced for every equivalent of hypochlorite decomposed. In the first experiment referred to it was found that 0·0462 equivalent of sodium hypochloride per litre had disappeared, and this should likewise be the amount of sodium chloride produced. The actual quantity was 0·0399 equivalent per litre. In the second experiment 0·0590 equivalent of sodium hypochlorite disappeared, whilst 0·0517 equivalent of sodium chloride was formed. The actual quantity of sodium chloride formed is therefore somewhat less than that calculated. This might be due to the production of free chlorine or sodium chlorate, or both. In order to test for the production of chlorine, the gas evolved during the reaction was collected and analysed. A solution approximately $N/10$ with respect to hypochlorite was exposed for twenty-four and a-half hours, the current being approximately 4 amperes and the uviol lamp placed at a distance of 2 cm. from the solution. No cooling arrangement was employed in this instance, the temperature thereby rising to 35°. The dissolved air was given off at an early stage, followed after two to three hours by fine bubbles of photochemically produced gas, the total volume of gas collected being 65 c.c. Using the ordinary Hempel apparatus, the gas was shaken with a solution of ferrous chloride acidified with hydrochloric acid, but no absorption took place, that is, no chlorine is evolved during the decomposition, although a small quantity might have been produced and retained in the liquid. On further treatment of the gas with ammoniacal cuprous salt, 60 c.c. were absorbed, leaving an inert residue, which was probably nitrogen from the air. The conclusion to be drawn from the analysis is therefore that oxygen is the main product of decomposition of the hypochlorite.

The solution was next examined for production of sodium chlorate. After exposure the hypochlorite remaining was destroyed by means of carbamide, and the chlorate estimated by Knecht's titanous chloride method. The quantity of chlorate in the original solution was found to be negligible. With the lamp immersed in the solution an exposure of four hours forty-five minutes was taken, the current being 4·25 amperes. It was found that the concentration of the sodium hypochlorite had decreased by 0·0470 equivalent per litre, whilst the increase in concentration of the sodium chloride was 0·0367 equivalent, leaving 0·0103 equivalent of chlorine to be accounted for. It was found that sodium chlorate was produced by exposure to the light, the quantity being 0·0056 equivalent per litre. This accounts for about one-half of the discrepancy between the decrease of hypochlorite and increase of chloride, leaving 0·0045 equivalent of chlorine per litre still to be accounted for. This quantity, which amounts to less than one-tenth of the hypochlorite decomposed, is probably due to volatile hypochlorous acid which is present owing to the hydrolysis of the hypochlorite.

The Active Range of Wave-lengths.

The lamp before being immersed as before was surrounded by zinc foil, and an exposure of four hours twenty minutes taken, the current being 4·25 amperes. No attempt was made to keep the solution cool, the temperature rising to 52°. The amount of hypochlorite originally present was 0·101 equivalent per litre, and the amount at the end of the exposure was found to be 0·100. There is therefore practically no change in the composition of the solution. This result was checked by covering the lamp with a fine coating of soot from burning benzene, the exposure and time being the same as in the preceding experiment. A sample of the original solution required for titration 10·4 c.c. of the arsenious oxide, whilst a similar sample taken at the close required 10·3 c.c. These results show conclusively that infra-red rays are without any measurable photochemical action on sodium hypochlorite solution. The reaction is therefore a true photochemical one, in that it is brought about by the waves of the visible and ultraviolet spectrum.

Absorption Spectrum of Sodium Hypochlorite Solution.

The stock solution (practically normal) is coloured greenish-yellow, showing that there is absorption in the blue and violet. Normal and decinormal solutions were examined spectrographically, using the iron arc with quartz lens and containing vessel. An exposure of ten seconds was given, the results being as follows:

Solution.	Thickness of layer, in cm.	Solution transparent up to $1/\lambda$.
N...	10	2530
	8	2565
	6	2603
	4	2640
	2	2690
	1	2765
N/10	10	2765
	8	2791
	6	2812
	4	2845 and from 4235 to 4280
	2	2912 ,, 4090 ,, 4400
	1	2966 ,, 3980 ,, 4400 ?

There is thus an absorption band in the ultraviolet. The light of wave-lengths shorter than the band is of no importance for the present purpose, since the uviol glass does not transmit this region. It will be observed from the above data that Beer's law is obeyed with respect to the two concentrations employed.

Some spectroscopic measurements were made also with the uviol lamp. With the uviol sheath the shortest wave-length transmitted was $\lambda=2900$ $(1/\lambda=3448)$; with the glass sheath the shortest wave-length is $\lambda=3344$ $(1/\lambda=2990)$. The main point of difference in the rays transmitted by the lamp with uviol and ordinary glass sheath respectively is that in the first case the strong double line $\lambda=3144$ $(1/\lambda=3180)$ is transmitted, this being absorbed by the hypochlorite, whilst the same line is practically entirely stopped by the glass.

Decomposition of Neutral Hypochlorite Solutions.

In the previous measurements of photochemical decomposition the solutions were alkaline. It was of interest to see if the reaction proceeded in the same way in the absence of alkali. For this purpose the solution was neutralised with hydrochloric acid. Before adding the methyl-orange it was necessary to destroy the hypochlorite, as this would bleach the indicator. This was effected by means of carbamide. From the acidity data thus obtained, the required amount of acid was added to a portion of the solution in which the hypochlorite was undestroyed, and the latter exposed to the lamp. With a current of 4·25 amperes the exposure lasted four and a-half hours, the temperature of the solution being kept at 25°. It was found that starting with a solution 0·079*N* with respect to hypochlorite, after the exposure the amount of hypochlorite destroyed was 0·036 equivalent per litre, the amount of chloride and chlorate produced being 0·03224 and 0·00294 equivalent per litre respectively. This leaves 0·00082 equivalent of chlorine unaccounted for. It was observed, however, that the gas evolved consisted partly of chlorine, so that the course of the reaction is less simple than in the alkaline solution. It will be observed that the formation of chlorate in the neutral solution is about one-half of that produced in alkaline solution. The solution was again titrated after the exposure, and no measurable increase in alkalinity or acidity could be observed.

Rate of Decomposition of Neutral Sodium Hypochlorite Solutions.

The Order of a Photochemical Reaction.—In general, the true order of a photochemical reaction can only be obtained if it proceeds in the dark at a measurable velocity; for it is clear that only when mass action is sufficient in itself to bring about the reaction has the order any definite chemical significance. In many cases, as in the present, the speed in the absence of light is too small for measurement. In such cases it is usual to write the simplest stoicheiometric equation and assume that this corresponds with the true mass-action effect. In the present instance the reaction would be either unimolecular, that is, $NaClO \longrightarrow NaCl + O$, or bimolecular, namely, $2NaClO \longrightarrow 2NaCl + O_2$. If, however, the nascent oxygen atoms united very rapidly with one another, as one may expect, the reaction would be a unimolecular one, as it is always the slowest of a series which determines the rate.

When the system is exposed to light and a photochemical decomposition results, the simple kinetic assumptions, by means of which it is usual to visualise the mass-action effect, are no longer applicable. Instead of having to take into account the probability of molecules coming into contact (the probability of which is as great in the absence as it is in the presence of light, although in the former case the reaction does not proceed with measurable velocity), we have to take into account the relation of the light energy absorbed to the concentration of the absorbing substance. It is not necessary, therefore, to introduce any considerations of the ordinary conception of mass action, but, instead, to assume the reaction velocity to be directly proportional to the absorbed light energy. As a conclusion from Beer's law, which we have seen is obeyed in the present instance, it is justifiable to put the absorbed light energy directly proportional to the concentration of the absorbing substance when the absorption is weak, as is the case for a dilute solution of hypochlorite. Likewise when the absorption is great or complete, the light absorption is independent of the concentration of the absorbing substance. Hence the velocity of a photochemical reaction is either directly proportional to the concentration of the absorbing substance (when its concentration is small) or independent of its concentration when the latter is great. In other words, we may either have an apparently "unimolecular reaction" corresponding with the equation $dx/dt = k(a-x)$ or a "zero molecular reaction" corresponding with the expression $dx/dt = k$. We can thus obtain velocity expressions without necessarily assuming the law of mass action.

In the following table are given the values of "k" corresponding with zero-, uni-, and bi-molecular reactions respectively for sodium hypochlorite decompositions, using the uviol sheath at 25°. Quantities of 10 c.c. at a time were withdrawn by means of a pipette, and titrated with arsenious solution. The bulk of the solution exposed being nearly 2 litres, no appreciable change is thereby made in the area exposed.

Current, 4·25 amperes in experiments *A*, *B*, *C*, and *D*.

(A) *Initial Concentration of* NaClO = 0·075*N*.

Time in hours.	$a-x$ (c.c.)	$k=x/t$.	$k=1/t\log_{10}\frac{a}{a-x}$.	$k=1/t\,\frac{x}{a(a-x)}$.
0	7·5	—	—	—
1	6·35	1·15	0·0723	0·0242
2	5·40	1·05	0·0718	0 0259
3	4·50	1·00	0·0739	0·0296
4·5	3·25	0·95	0·0807	0·0387

(B) *Initial Concentration of* NaClO = 0·0742*N*.

Time in hours.	$a-x$ (c.c.).	$k=x/t$.	$k=1/t\log_{10}\frac{a}{a-x}$.	$k=\frac{x}{ta(a-x)}$.
0	7·42	—	—	—
1·33	6·00	1·07	0·0692	0·024
2·66	4·75	1·00	0·0726	0·028
4·0	3·80	0·905	0·0726	0·032
6 0	2·70	0·95	0 0732	0·039

At the close of this experiment the lamp was turned off for sixteen hours, and the final titration again carried out. The value obtained was 2·65 (instead of 2·70), so that in the decomposition of sodium hypochlorite no measurable "after-effect" is observed.

(C) *Initial Concentration of* NaClO = 0·0735*N*.

Time in hours.	$a-x$ (c.c.).	$k=x/t$.	$k=1/t\log_{10}\frac{a}{a-x}$.	$k=\frac{x}{ta(a-x)}$.
0	7·35	—	—	—
1	6·38	0·97	0 0615	0·0239
2·5	4·90	0·98	0·0705	0·0285
4·5	3·80	0·79	0·0636	0·0282
5 75	3·15	0·73	0·0640	0·0320

(D) *Initial Concentration of* NaClO = 0·075*N*. In this experiment a different uviol sheath was employed.

Time in hours.	$a-x$ (c.c.).	$k=x/t$.	$k=1/t\log_{10}\frac{a}{a-x}$.	$k=\frac{x}{ta(a-x)}$.
0	7·50	—	—	—
1	6·40	1·10	0·0690	0·023
2·5	5·18	0·93	0·0643	0·053
4·5	3·62	0·86	0·0703	0·030
6·0	2·80	0·78	0·0713	0·022

The zero-molecular constant, $k=x/t$, in all cases shows a steady fall with time, although the range over which the concentration change was observed is not wide enough to show if the discrepancy becomes great when the solution is very dilute. In the first three cases the bimolecular constant shows a steady rise with time; in the fourth it varies irregularly. The unimolecular constant varies irregularly in general, although here also there seems to be a tendency to rise. For the present, the reaction will be treated as a unimolecular one, although it is recognised that this requires further confirmation. The mean unimolecular constant for (*B*), (*C*), and (*D*) is:

$$k = 0{\cdot}0685.$$

In the above treatment it has been assumed that the reaction proceeds completely in the direction $NaClO \longrightarrow NaCl + O$. This was shown to be the case by exposing a solution continuously for twenty-one hours, after which a barely perceptible coloration was obtained with potassium iodide and starch. Two drops of arsenious oxide solution added to the sample of solution withdrawn were sufficient completely to remove the remaining hypochlorite. The reaction may therefore be regarded as practically completing itself—a result to be expected, since one of the products of decomposition, namely, oxygen, is being continuously removed from the system.

In the velocity determinations quoted, the current in the lamp was kept at 4·25 amperes. The following measurements were carried out with a current of 3·5 amperes, using the uviol sheath as before:

(E) *Initial Concentration of* $NaClO = 0{\cdot}0747N$.

Unimolecular constants: 0·0611, 0·0596, 0·0612; mean, 0·0606.

(F) *Initial Concentration of* $NaClO = 0{\cdot}075N$.

Unimolecular constants: 0·0622, 0·0619, 0·0599, 0·0602; mean, 0·0610.

Mean of (*E*) and (*F*) = 0·0608.

With a current of 4·25 amperes the constant obtained is 0·0685. There is therefore an increase in the constant with the current, the proportionality factor in the two cases being 0·016 and 0·017 respectively.

Rate of Decomposition of the Neutral Solution when a Glass Sheath is Interposed.

With a current of 3·5 amperes in the lamp the following unimolecular constants were obtained:

(*G.*)	(*H.*)	(*I.*)	(*K.*)	
0·0408	0·0419	[0·0447]	0·0403	Mean, $k = 0{\cdot}0395$
0·0374	0·0408	0·0397	0·0380	
0·0393	0·0403	0·0386	0·0373	

On comparing these values with those of experiments (*E*) and (*F*) one obtains the following relation:

$$\frac{\text{Photochemical effect through uviol glass}}{\text{Photochemical effect through ordinary glass}} = \frac{0{\cdot}0608}{0{\cdot}0395} = 1{\cdot}54.$$

If we write:

Total effect through uviol = total effect through glass + extra ultraviolet region transmitted by uviol,

it will be seen that the photochemical action due to the extra ultraviolet region transmitted by the uviol amounts to 35 per cent. of the whole. No direct comparison can be drawn, however, regarding the photochemical efficiency of a given region until the values are reduced to the same energy standard by means of thermopile measurements (Ladenburg, *Physikal. Zeitsch.*, 1904, **5**, 525).

Rate of Decomposition of Alkaline Solutions of Sodium Hypochlorite.

The uviol sheath was employed as before, the current in the lamp being 3·5 amperes:

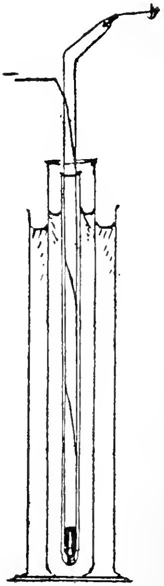
Initial concentration of NaClO = 0·07*N*.

Concentration of NaOH = 0·0019*N*.

The following unimolecular constants were obtained:

0·0496	0 0475	0·0529	0·0536	
[0·0447]	0·0473	0·0462	0·0497	Mean, $k = 0{\cdot}0494$
0·0479	0·0476	0·0491	[0·0563]	
			0·0525	

The velocity-constant is considerably lower than that corresponding with the neutral solution; in other words, the alkaline hypochlorite is the more stable.



Effects Produced by the Interposition of Coloured Liquids.

In addition to the uviol sheath which protected the lamp, another of wider bore was placed round the first, the coloured liquid being poured between. The thickness of the layer which the light had to traverse was 1 cm. The hypochlorite solution was in contact with the outer uviol cylinder. The arrangement will be easily understood with the aid of the figure.

Effect of Layer of Distilled Water.—Alkaline hypochlorite approximately *N*/10; current in lamp, 3·5 amperes; unimolecular constants:

0·0440	0·0458	
0·0457	0·0467	Mean, $k = 0{\cdot}0456$
0·0458	—	

It will be noted that the "*k*" apparently shows an increase with time. The value of "*k*" obtained in the absence of the water layer was 0·0494, so that the absorption caused by 1 cm. of water reduces the constant to 92 per cent. of its former value. In measurements with other absorbing layers (aqueous solutions) the effect due to the solvent and solute separately can thus be isolated at least approximately.

Effect of Layer of Aqueous Potassium Ferrocyanide.

Concentration of $K_4Fe(CN)_6$ in equivalents per litre.	Unimolecular constant of decomposition of sodium hypochlorite.	
1	0	
0·5	0	
0·2	<0·002	
0·1	0·0071, 0·0057	mean, 0·0064
0·05	0·0085, 0·0055	,, 0·0070
0·01	0 0150, 0·0135, 0·0117	,, 0·0134
0·01 (continuation of preceding measurement after 5 hours' exposure)	0·0081, 0·0055	
0·001	0·0298, 0·0399	mean, 0·0348
0·0	0·0494	

These results show the applicability of the Grotthus-Draper law, according to which it is the light that is (optically) absorbed which is, in part at least, photochemically active, the ferrocyanide solution having absorption in the same region as the hypochlorite. A serious drawback to the use of potassium ferrocyanide for this purpose is the fact that it itself is decomposed, the solution becoming turbid and therefore more opaque with time. This is very probably the cause of the fall in "*k*" with time; and for the same reason the values ought to be extrapolated to zero time, although the data here obtained were not considered sufficiently accurate for this purpose. It will be observed that the more dilute ferrocyanide solutions are proportionately more effective than the more concentrated. To test the Grotthus-Draper law more rigidly, a portion of the hypochlorite solution itself (0·16*N*) was employed as the absorbing screen. The following values were obtained:

Time, in hours.	*k*.	
0	—	Mean, 0·0150
2	0·0124	
4	0·0151	
6	0·0153	
8	0·0147	

During this exposure the concentration of the outer hypochlorite decreased in the ratio of 16·2 : 12·35. The decrease in the concentration of the screen would naturally be greater, but was not determined. The value of k appears to become fairly constant after a time. One would have expected that there should have been a rise of k with time, owing to the decomposition of the inner hypochlorite. Further experiments upon this subject are in progress.

Discussion of Results.

We have already seen that in photochemical reactions the law of mass action in its usual form may not necessarily be the cause of the reaction. A velocity constant (limited to a "uni-" or "zero"-molecular one) may be obtained theoretically by taking into consideration the quantity of light absorbed. In the present case, even in the dark, there is a slight decomposition of the hypochlorite, evidently of the same nature as the decomposition in the light. The light therefore acts as a catalyst. From a theoretical point of view such reactions are not as interesting as those in which the light does work against the chemical (mass action) forces, as in the case of the polymerisation of anthracene (Luther and Weigert, *Zeitsch. physikal. Chem.*, 1905, **51**, 298; **53**, 416). In the present instance the chief interest lies in the mechanism of the photocatalytic process. In this connexion it seems pertinent to draw attention to the phenomenon of sensitisation, in which, for example, a substance such as silver chloride can be made photosensitive to red rays by being impregnated with a dyestuff which absorbs red. Weigert has shown that in a gaseous system a similar phenomenon may be observed, as in the sensitisation of ozone to the blue rays by the addition of chlorine, which absorbs these rays. Similarly, many instances of sensitisation are observed in the case of substances in solution, for example, sensitisation of toluene by bromine. The phenomenon is thus a very general one. The simplest physical conception of the process is that the electrons of the coloured substance (the sensitiser) vibrate in unison with the ether vibrations corresponding with the complementary colour possessed by the sensitiser, and by the absorption of the light these electrons are set into more violent vibration. This increased vibrational energy tends to cause forced vibration of the same period in the electronic systems of neighbouring molecules, the latter being thus chemically sensitised to the same wave-lengths as the sensitiser itself. It does not seem, however, to have been suggested that such sensitisation might manifest itself as an auto-effect in the different layers of a light-absorbing medium. Such an effect would afford an explanation of photocatalysis in general, and at the same time would not be in disagreement with the conclusions already reached, according to which a photochemical reaction should be apparently uni- or zero-molecular.

Summary.

(1) Aqueous solutions of sodium hypochlorite, both neutral and alkaline, may be photochemically decomposed by the light from a mercury-vapour uviol lamp, the principal products of decomposition being sodium chloride and oxygen.

(2) The reaction cannot be brought about with measurable velocity by means of infra-red rays, the effective region being that of the visible and ultraviolet. A comparison of these regions is attempted by using sheaths of ordinary glass and uviol glass respectively.

(3) The hypochlorite solutions show a marked absorption band in the ultraviolet.

(4) The photochemical reaction proceeds at a measurable rate, the order being provisionally taken as unimolecular.

(5) By means of light filters consisting of potassium ferrocyanide solutions of various concentrations, it is shown that by cutting off the blue and violet along with the ultraviolet the velocity of the reaction is reduced to zero. The Grotthus-Draper law is further supported by the observed decrease in velocity when some of the hypochlorite solution itself is used as a filter.

(6) Finally, the results are discussed from the point of view of photocatalysis.

In conclusion, the writer's best thanks are due to Dr. W. B. Tuck for photographing and measuring the absorption spectra of the solutions, and likewise to Mr. E. M. Lake for some assistance with the analytical portion of the work. The author also wishes to acknowledge his indebtedness to the Government Grant Committee of the Royal Society for a sum which covered the expenses of the investigation.

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CCLI.—*Inositol and Some of its Isomerides.*

By Hugo Müller.

In the present communication I propose to give an account of the further extension of the investigation of inositol * and some of its isomerides, of which I have already published a preliminary part (Trans., 1907, **91**, 1767). As the work to be described comprises a number of separate investigations, it will be most convenient to preface the detailed description of the experimental work with a brief summary of the results which have been obtained.

The literature of this subject contains the description of several isomerides of inositol. Staedeler and Frerichs (*J. pr. Chem.*, 1858, **73**, 48) obtained a substance from the kidneys and other organs of certain plagiostomous fishes which they named "scyllite"; Vincent and Delachanal (*Compt. rend.*, 1887, **104**, 1855) isolated a substance of the same composition from the mother liquors of the preparation of quercitol from acorns, and called it "quercine"; and I myself isolated from the leaves of *Cocos plumosa* and *Cocos nucifera* a substance resembling inositol in chemical character and having the same composition, to which I gave the name "cocosite" (*loc. cit.*).

A consideration of the properties of scyllite and quercine had already led me to the conclusion that it was possible that these substances were identical with cocositol, and I therefore called attention to this possibility in a previous paper (*loc. cit.*, p. 1780). With the object of deciding this important point I prepared a specimen of scyllite from *Acanthias vulgaris* (the spur dogfish), and M. Delachanal was good enough to send me some of the original specimen of quercine from the collection of the late M. Vincent. It therefore became possible to make a direct comparison of the chemical and crystallographical properties of these substances and cocositol (p. 2388), with the result that there can now be no doubt that these three substances are identical. Since the first to be discovered was scyllite, the names "quercine" and "cocositol" are no longer needed, and these three substances, derived from these different sources, will in future all come under the heading "scyllitol." In the earlier research on inositol, to which reference has already been made, a study of the action of a

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* The inositol used in these experiments was the inactive modification which had been obtained from the mother liquors of the preparation of the dye-stuff cochineal, and was part of the same material which had been employed in the previous investigation.

solution of hydrogen bromide in glacial acetic acid on inositol hexa-acetate was undertaken, and resulted in the following substances being isolated in a pure condition:

	M. p.
Monobromoinositol penta-acetate, $C_6H_6Br(O{\cdot}CO{\cdot}CH_3)_5$	240°
Dibromoinositol tetra-acetate, $C_6H_6Br_2(O{\cdot}CO{\cdot}CH_3)_4$.............. (scaly modification)	235
Dibromoinositol tetra-acetate, $C_6H_6Br_2(O{\cdot}CO{\cdot}CH_3)_4$...... .... (massive modification)	140
Inositoldibromohydrin, $C_6H_6Br_2(OH)_4$	210
Inositolbromohydrin,* $C_6H_6Br(OH)_5$	175

* This substance is described for the first time in the present communication p. 2398).

In continuing these experiments, interesting results have been obtained as the result of the study of the behaviour of inositol hexa-acetate as well as of inositol itself with a solution of hydrogen iodide and hydrogen chloride in acetic acid at elevated temperatures.

When inositol hexa-acetate is heated with an acetic acid solution of hydrogen chloride for several hours at 150—160°, it yields invariably a complex mixture of the following chlorinated derivatives; and it deserves notice that in this reaction no dichlorinated derivatives are formed:

	M. p.
α-Inositolchlorohydrin penta-acetate, $C_6H_6Cl(O{\cdot}CO{\cdot}CH_3)_5$	247°
β-Inositolchlorohydrin penta-acetate, $C_6H_6Cl(O{\cdot}CO{\cdot}CH_3)_5$	110
γ-Inositolchlorohydrin penta-acetate, $C_6H_6Cl(O{\cdot}CO{\cdot}CH_3)_5$	118
Inositolchlorohydrin triacetate, $C_6H_6Cl(OH)_2(O{\cdot}CO{\cdot}CH_3)_3$	145
Inositolchlorohydrin, $C_6H_6Cl(OH)_5$	185

Perhaps the most interesting result of the present investigation, however, is the fact that the product of the interaction of hydrogen iodide and the mother liquors from these chloro- and bromo-derivatives contains two new modifications of inositol, which have been named iso*inositol* and *ψ-inositol.*

iso*Inositol* crystallises in transparent crystals, which were sufficiently well developed to allow of accurate crystallographical measurement (p. 2401). It melts at 244°, and is more soluble in water than inositol; on treatment with acetic anhydride it yields a *hexa-acetate*, which crystallises in massive prisms and melts at 112°.

ψ-Inositol differs from all the other isomerides in being excessively soluble in water, with which, indeed, it mixes in all portions. When treated with acetic anhydride, it yields an amorphous *acetyl* derivative, gives the Scherer inositol reaction, and in other of its chemical properties exhibits similarity to inositol. The isolation of these two new modifications of inositol from the mother liquors of the action of hydrochloric acid (and also of hydrobromic acid and hydriodic acid, compare pp. 2399, 2407) on inositol or its hexaacetate raises the question whether the brominated and chlorinated derivatives described in this and the previous communication are actually derivatives of inositol or whether they may not possibly be derivatives of *iso*inositol or ψ-inositol. This point might conceivably have been decided in two ways, namely, (i) by regenerating the parent substances from the halogen derivatives by hydrolysis, but all attempts to accomplish this have failed; or (ii) by acting on the acetates of *iso*inositol and ψ-inositol with acetic acid solutions of the halogen acids, and comparing the products with those obtained from inositol directly. The latter process would not necessarily have given valid results, and in any case it could not be carried out owing to the small amounts of these new isomerides which were available. The exact derivation of these halogen derivatives must remain, therefore, in the meantime undecided, and, until conclusive evidence to the contrary is forthcoming, it will be assumed that they are derived from inositol.

Another point of interest which has been observed during the course of the present investigation is the curious fact that scyllitol (cocositol), which differs so markedly from inositol in many ways, and particularly in its physical properties, when subjected to the action of hydrogen chloride or bromide or iodide in acetic acid solution, always yields exactly the same substances as are produced from inositol under the same conditions. Obviously, at some stage in the series of reactions intramolecular change, either of the scyllitol into inositol or vice versa, or of both of them into some common substance, such as *iso*inositol, for example, must take place, and it is possible that the rather high temperature which has usually to be employed in order to bring about interaction may play a prominent part in inducing the change of configuration.

I am indebted to Prof. W. H. Perkin for the analyses of the various substances, carried out at the Schunck Laboratory, Victoria University, and also to Mr. T. V. Barker, of the Mineralogical Department, University Museum, Oxford, who has kindly undertaken the crystallographical examination of the compounds which are described in this communication.

EXPERIMENTAL.

The Identity of Scyllitol, Cocositol, and Quercine.

In the former paper on cocositol and inositol (Trans., 1907, **91**, 1780) I called attention to the remarkable resemblance of cocositol to scyllitol, a substance discovered some fifty years ago by Staedeler and Frerichs (*J. pr. Chem.*, 1858, **73**, 48) in the kidneys and other organs of certain plagiostomous fishes, and recently again prepared from the same source and more fully examined by Johannes Müller (*Ber.*, 1907, **40**, 1821). This close resemblance made it very desirable to determine whether cocositol and scyllitol, although derived from such widely different sources, are, in fact, identical, and not, as had hitherto been supposed, isomeric modifications of the prototype inositol, and in order to institute a careful comparison it was necessary to obtain a supply of pure scyllitol. For the purpose of preparing this substance it was found that the *Acanthias vulgaris* (spur dogfish) was the most readily obtainable material, but, as some difficulty was experienced in obtaining the necessary quantity of the particular organs in a perfectly fresh condition, it was decided to experiment, in the first instance, with the substance of the entire fish. The process adopted, which was found to work satisfactorily, may be briefly described as follows: Fifty kilos. (thirty-four fishes) of *Acanthias vulgaris*, after being crushed to a pulp, were repeatedly extracted with cold water, and the liquid was separated from the insoluble part by pressure and filtration. The liquid was then reduced by evaporation to about 10 litres, and, after cooling, filtered and precipitated with excess of neutral lead acetate, again filtered, and the bulk further reduced to 8 litres. At this stage it was considered desirable to test the efficiency of two different methods of procedure, and for this purpose the liquid was divided into two equal parts. The one-half was treated with basic lead acetate according to the method originally used by Staedeler and Frerichs (*loc. cit.*), and the other half was treated with barium hydroxide under conditions which I had worked out during my experiments on the preparation of cocositol from cocos palm leaves (Trans., 1907, **91**, 1771). The addition of the basic lead acetate produced a bulky precipitate, which was washed with cold water by decantation and filtration, and then stirred with dilute acetic acid, which dissolved nearly the whole, leaving only some lead chloride and phosphate. The solution was precipitated with sulphuric acid, leaving a small amount of lead in solution, and, after filtering, the lead in solution was removed with hydrogen sulphide, the liquid was again filtered, evaporated on the water-bath to a small volume, and, after treatment with animal charcoal, further concentrated, when, on cooling, the scyllitol crystallised, and on mixing the mother liquor, while hot, with alcohol a further small quantity was obtained, amounting together to 1·8 grams. The other half of the original extract was freed from lead, and then evaporated to about 1 litre, and, while boiling, mixed with a hot concentrated solution of barium hydroxide, which caused a heavy, copious precipitate. The whole was boiled for a short time, the precipitate collected, washed with hot water, and treated with carbon dioxide exactly as described in the preparation of cocositol (Trans., 1907, **91**, 1771). On evaporating the filtrate from the barium carbonate to a small bulk, a pale yellow, amorphous substance first separated, which proved to be guanine, and the still further concentrated liquid, while evaporating on the water-bath, began to form brilliant crystals, which on cooling became mixed with a crystalline substance less definite in character. The latter appeared to be a mixture of sarcine (hypoxanthine) and xanthine, which were readily removed by washing the crystals, first with dilute hydrochloric acid, and then with dilute alcohol. The yield of this second half of the extract amounted to 1·9 grams; thus, in all, 3·7 grams of scyllitol were obtained from the 50 kilos. of fish. This is about the same proportion which had been previously obtained when the particular organs only were used (*Ber.*, 1907, **40**, 1821), and it would therefore appear that the scyllitol occurs to the same amount in the muscle of the fish. A special search for inositol which was made failed to detect its presence.

Considering the smallness of the yield it is well to bear in mind that a special experiment showed that the whole of the aqueous extract from the 50 kilos. of fish contained only about 400 grams of solid matter (dried at 120°).

The whole of the product was finally dissolved in water, treated with animal charcoal, and recrystallised. As on the former occasion when working with cocositol on a somewhat larger scale, it was noticed that the best-developed crystals were obtained by evaporating the solution at or near the boiling point on a water-bath or otherwise, and adding fresh solution as the evaporation proceeds.

As soon as crystallisation began, the striking similarity to cocositol manifested itself in the manner in which the crystals formed in the hot liquid. When, on the other hand, crystallisation took place at the ordinary temperature, the same hydrated crystals which turn white on exposure were found to be intermixed with the anhydrous, as has also been noticed to be the case with cocositol. Otherwise, the scyllitol behaved in every respect like cocositol, and when acetylated furnished the hexa-acetate, which possessed all the characteristic properties of cocositol hexa-acetate.*

Mr. T. V. Barker kindly undertook the measurement and deter-

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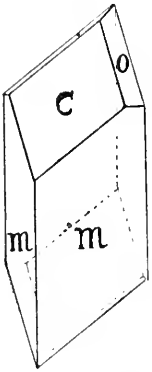
* A previous experiment, made on a somewhat larger scale, did not yield a trace of scyllitol. It was then discovered that, probably by inadvertence, instead of the organs of the plagiostomous fishes, those of ordinary food fishes had been used. The material used in the present research was obtained with the assistance of the Marine Biological Association at Plymouth, and the preparation of the extract was carried out for me in the pharmaceutical laboratory of Mr. W. Martindale.

mination of the crystals of scyllitol, and the results are given in the following table with those formerly obtained by him with cocositol and also with Friedel's measurement of quercine (see p. 2398).

Scyllitol.

Scyllitol is crystallographically identical with the cocositol formerly measured (Trans., 1907, **91**, 1772), so that there can be no doubt concerning their chemical identity. Moreover, a comparison of the measured angles given later will prove that the "quercine" measured by Friedel (*Compt. rend.*, 1887, **105**, 95) is also identical with scyllitol.

Fig. 1.



Scyllitol (identical with cocositol and quercine).

The habit and forms exhibited by "scyllitol" and cocositol are precisely the same, with the exception that the form $r-\{\bar{2}01\}$ previously noted on cocositol was not observed in scyllitol; but this slight difference is, of course, of no consequence, inasmuch as the appearance or suppression of a single form depends greatly on accidental circumstances attending crystallisation. A typical crystal of scyllitol is shown in Fig. 1.

Two crystals were measured on the two-circle goniometer, and it is seen that the results obtained are in agreement with those deduced from the crystal constants formerly given for cocositol, namely:

System: Monoclinic.

Ratios of the axes: $a:b:c=1{\cdot}7942:1:0{\cdot}7656$; $\beta=117°12'$.

Table of Measured and Calculated Angles.

		Measured.		Calculated.	
Face.	No.	ϕ.	ρ.	ϕ.	ρ.
$m=110$	4	32° 2′	—	32° 4½′	—
$c=001$	1	90 8	27° 0′	90 0	27°12′
$o=111$	2	2 13	37 28½	2 36	37 28

The cleavage is the same as for cocositol, namely, parallel to $c-(001)$; the optical properties, too, point to the identity of the two substances. Two determinations of the specific gravity gave a mean value of D_4^{19} 1·659; this agrees within the limits of experimental error with the value formerly given for cocositol, D 1·660.

The identity of quercine with scyllitol and cocositol is obvious from the description given by Friedel. The form combination was the same, and the angles observed were very close, the constants deduced by Friedel being:

$$a:b:c = 1{\cdot}8096:1:0{\cdot}7690;\ \beta = 117^\circ 39'.$$

Quercine.—At an early stage in my investigation of cocositol (Trans., 1907, **91**, 1767) I recognised its resemblance to quercine, a substance discovered by Vincent and Delachanal (*Compt. rend.*, 1887, **104**, 1855), and occurring in very small quantity in the mother liquors of the preparation of quercitol from acorns. This suggested the probability of its presence in the leaves of *Chamaerops* species, in which I had recognised the occurrence of quercitol in considerable quantities, and which, indeed, serve as a convenient source for the preparation of this substance. In order, therefore, to obtain some quercine, I worked up a supply of leaves obtained from Kew, but failed to find any indication of quercine being associated with quercitol in this plant. Having in the meantime demonstrated the identity of cocositol with scyllitol, it became all the more desirable to determine whether quercine is an individual substance or is also identical with scyllitol, and therefore I addressed myself to M. Delachanal, who kindly furnished me with a specimen of the original quercine from the collection of the late M. Vincent.

I was thus in a position to make a close comparison of this substance with scyllitol, and the result leaves no doubt that these two substances, derived from such different sources, are identical.

In order to prove this point with the small quantity of material available, the exact comparison of the melting points was selected as likely to give the most trustworthy result. In my paper on cocositol (*loc. cit.*, p. 1772) I have referred to the difficulty experienced in the determination of its melting point due to the high temperature of fusion, and the consequent untrustworthiness of the mercury thermometer.

For the present purpose it was therefore considered desirable to employ thermo-electric measurement, and I have to thank Dr. W. Wahl for the assistance he kindly gave me in carrying out these experiments.

The apparatus consisted of a Jena-glass tube 20 cm. long and 25 mm. internal diameter, containing a mixture of potassium and sodium nitrates which formed the bath, and this was electrically heated by a platinum wire of 0·2 mm. thickness and 3·5 metre length coiled externally round the tube. A current of 2·2 amperes was passed through this wire, and the temperature was regulated by means of a sliding resistance.

The tube was fixed in an Argand lamp cylinder by means of asbestos, and was provided with an efficient stirrer, and the perfectly clear and colourless bath allowed observation of the melting point of the substance, which was contained in a thin glass tube, being watched with a telescope from a distance, whence also the stirrer was worked. The temperature was measured by means of a thermo-couple of platinum and rhodium-platinum, the wires of which were 0·2 mm. thick, and these were enclosed in a Berlin porcelain tube of 3 mm. internal diameter, closed at the end.

One of the wires was contained in a capillary porcelain tube of about 1 mm. diameter, and thus isolated. The reading of the temperature was made with a Siemens and Halske direct-reading galvanometer placed close to the telescope. For the purpose of standardising the thermo-couple the temperature scale of the Carnegie Institute (B. Sosman, *Amer. J. Sci.*, 1910, [iv], **30**, 126) was employed, and the necessary corrections were found to be those given in the following table:

	M. p.	Thermo-couple.	Correction.
Cadmium	320·2°	305·8°	+14·4°
Zinc	418·2	398·5	19·5
Antimony	629·2	598·5	30·7

During the actual determination of the melting points of quercine, scyllitol, and cocositol, it was observed that, immediately before fusion, the inner part of the tube above the substance turned slightly brown, and that the substance, in the act of melting, frothed up. This behaviour was exactly the same with all three substances, and took place when the galvanometer indicated for quercine 334°, for cocositol 335°, and for scyllitol 333·5°, and after adding to these numbers the required correction of 15°, the melting points obtained are for quercine 349°, for cocositol 350°, and for scyllitol 348·5°. Although this behaviour may be taken as strong evidence of the identity of these three substances, it was thought wise to compare the hexa-acetates also, more especially because their melting points are considerably lower. In order to do this it was necessary to convert the small quantity of quercine into the hexa-acetate, when it was noticed that, in its mode of formation and in its crystalline character, it exhibited the closest resemblance to the hexa-acetates of cocositol and scyllitol.

The determination of the melting points of the three hexa-acetates in the apparatus described above gave the following results:

	M. p. observed.	Correction.	True m. p.
Scyllitol hexa-acetate	278—279°	+12°	290—291°
Quercine ,,	278	—	290
Cocositol ,,	277—278	—	289—290

The observed melting point of a mixture of scyllitol and cocositol hexa-acetates was 278°, or, corrected, 290°, and that of a mixture of quercine and cocositol hexa-acetates was 278° and 290° respectively.

It was furthermore observed that, in all three cases, some of the substance sublimed in glistening crystals.

Action of Hydrogen Iodide on Inositol Hexa-acetate.

All attempts at effecting by a suitable reaction the replacement of the bromine in the brominated derivatives of inositol hexa-acetate (Trans., 1907, **91**, 1782) having so far failed, it was thought desirable to ascertain the behaviour of the corresponding iodine compounds if such were obtainable. In was known that ordinary concentrated hydriodic acid, when heated with inositol, acted very readily; but in these circumstances the inositol was completely decomposed into phenol and benzene. Nevertheless, it was conceivable that a saturated solution of hydrogen iodide in glacial acetic acid when acting on the hexa-acetate might act differently and give more favourable results.

It was found, however, that although hydrogen iodide employed in this form would act on the hexa-acetate, none of the desired iodine derivatives was formed. Notwithstanding this disappointment, these trials led to other interesting results, an account of which is given in the following.

The hexa-acetate is acted on already at the temperature of the boiling-water bath, as is indicated by the copious liberation of iodine; but, as might be expected, this involves a partial decomposition, which, indeed, is manifested by the production of phenol, iodophenolic compounds, and other less defined dark-coloured substances; thus a very considerable portion of the material is virtually destroyed. The part, however, which escapes destruction consists mainly of two new isomeric forms of inositol and their acetates.

Of these new forms of inositol, to which, for the present, the names of iso*inositol* and ψ-*inositol* may be assigned, the one is well crystallised, whilst the other, until quite recently, had been obtained only in an amorphous state.

In carrying out the investigation, a series of preliminary experiments was made, and as the result of these the following procedure was finally adopted.

Inositol hexa-acetate, in quantities of 25 grams, was heated with 50 c.c. of glacial acetic acid saturated with hydrogen iodide in a sealed tube in the water-bath for five hours, by which time the contents of the tube had changed to a deep orange colour, but in order to complete the reaction as far as possible the heating was continued for a further fourteen hours. The tubes after cooling were then found to contain much crystallised iodine mixed with crystals of unchanged hexa-acetate. The whole product was transferred to a retort and distilled to dryness under diminished pressure, when it was noticed that the distillate contained some phenol, which was identified by means of its tribromo-derivative. The residue in the retort was boiled with much water, and the dark, insoluble portion which contained iodine and unchanged hexa-acetate was rubbed with aqueous sulphurous acid, and, after drying, digested with boiling alcohol, to which it imparted an olive-green colour. The alcoholic extract on cooling deposited unchanged hexa-acetate and some more after distilling off the greater part of the alcohol, which in one experiment amounted altogether to 15 per cent. of the quantity employed. The dark substance insoluble in alcohol was ultimately obtained as a purple-brown powder, which contained some iodine. This substance closely resembles the brown colouring matter noticed as one of the products of the action of hydrogen bromide on scyllitol hexa-acetate; it is partly soluble in alcohol, and also in alkali with a reddish-violet colour, but, being amorphous, it was not further investigated. The only other substance containing iodine which was present in the product of the reaction was iodophenol, which was recognised by its penetrating and characteristic odour.

The concentrated olive-green alcoholic extract after having been decolorised with animal charcoal was evaporated, when a viscid residue was left, which melted in hot water to a heavy oil, and on examination proved to be an acetate, readily hydrolysed by a boiling solution of barium hydroxide or when heated with concentrated hydrochloric acid. By these means a semi-crystalline substance was finally obtained, which was readily soluble in water, and consisted, as will be shown further on, of a mixture of the new isomerides.

The aqueous extract, obtained as described above, was evaporated on the water-bath, filtered, and again evaporated, and this process was repeated several times in order to separate some of the above-mentioned acetates, together with some of the colouring matter which had been retained in solution by the acetic acid present. Finally, the solution was treated with animal charcoal and evaporated, when a colourless, viscid residue remained, which gradually became opaque and semi-crystalline; to all appearance this was identical with the product obtained by hydrolysing the acetates referred to above, and, accordingly, they were mixed together. In order to remove acetic acid which was still present, the mixture was now heated for some hours at 130°, and it was then found that it amounted to 16 per cent. of the inositol hexa-acetate which had been employed. The mass, which was now brittle and glassy and became opaque and crystalline in a few days, was dissolved in just sufficient water, and, while hot, alcohol (98 per cent.) was gradually added. This caused at first a milkiness and then a heavy, oily liquid separated, which solidified on cooling, and in a few days became crystalline, and at the same time the alcoholic mother liquor was filled with a mass of small, white crystals. Closer examination showed that two different kinds of crystals were present, namely, slender prisms of ordinary inositol, and larger, massive crystals, which were at first thought to be one of the wished-for iodine derivatives, but which proved to be free from iodine. As these substances could not be directly separated, advantage was taken of the marked difference in the solubility in alcohol of their acetates, a fact discovered as the result of a preliminary experiment. The mixture was acetylated in the usual manner with the aid of a little zinc chloride, and the heavy, oily product dissolved in hot alcohol, when on keeping in the ice-box, crystals of inositol hexa-acetate gradually separated. The small quantity of inositol which adhered with such persistence to the product was thus finally removed, and the other acetate contained in the alcoholic mother liquor was once more hydrolysed. The isolation of the *iso*inositol was not, however, yet complete, as there was another substance (ψ-inositol) which had to be removed, and although the greater part of this had been retained in the mother liquor when the aqueous solution of the crude product was precipitated with alcohol, some of it still remained with the inositol. By a laborious process of fractional precipitation of the aqueous solution with alcohol and final crystallisation by the spontaneous evaporation of the solution at the ordinary temperature, the substance was obtained in a pure state and analysed:

0·1240 gave 0·1735 CO_2 and 0·0780 H_2O. C = 38·1; H = 7·0.

$C_6H_{12}O_6 + \frac{1}{2}H_2O$ requires C = 38·1; H = 6·9 per cent.

This substance has therefore the composition of inositol, and, as a close comparison proved, shares its general chemical properties; but, on the other hand, differs in its physical properties. It is therefore to be regarded as a new isomeride of inositol, and has been named *iso*inositol. In order to avoid repetition, the fuller description of its properties will be given when dealing with the product of the action of hydrogen chloride on inositol hexa-acetate and on inositol in the free state (p. 2399).

This will be also the case with the description of the substance associated with *iso*inositol, and which on account of its great similarity in its properties caused so much difficulty in the process of separation. At this stage it was only considered a troublesome by-product; later on, however, when the hydrogen chloride process provided ampler material, it was recognised as another isomeride and called ψ-inositol (p. 2404).

Action of Hydrogen Chloride on Inositol Hexa-acetate.

In view of the results of the foregoing investigation it seemed of interest to ascertain in a similar way the behaviour of inositol hexa-acetate when submitted to the action of hydrogen chloride. It had been observed that hydrogen chloride in glacial acetic acid solution reacts with much less readiness on inositol hexa-acetate than a similar solution of hydrogen bromide or hydrogen iodide, and, even after prolonged heating at a high temperature, a considerable proportion of the hexa-acetate usually remains unchanged. Several preliminary experiments were therefore necessary before the most favourable conditions of interaction could be discovered, but ultimately the following process was adopted as yielding satisfactory results. Inositol hexa-acetate (25 grams) is heated in a sealed tube with glacial acetic acid * saturated with hydrogen chloride at the ordinary temperature (60 c.c.) for fifteen hours at 150—160°. The colourless liquid contents of four such tubes were poured into a flask, and left in the refrigerator overnight, when a small quantity (2·4 grams) of minute crystals had separated; these were collected and found to consist of unchanged hexa-acetate and α-inositolchlorohydrin penta-acetate. The liquid was now distilled under diminished pressure in order to remove the hydrogen chloride and acetic acid as far as possible, and the hard, brittle residue, which still contained acetic acid, was extracted six times with boiling water (1200 c.c. in all), which dissolved part of it and left 58 grams of an oily liquid which, on cooling, became a glassy solid (*B*). The aqueous extract became milky on cooling, and deposited a semicrystalline substance, and on concentrating the liquid on the water-bath, heavy, oily drops formed, which collected at the bottom of the vessel and became a semi-transparent, brittle mass when cold. As these substances closely resembled the above undissolved 58 grams of glassy solid (*B*) they were added together. The original product was, by this treatment, roughly divided into a portion readily soluble in water (*A*), and a second much less soluble portion (*B*), and, at the same time, during the evaporation the greater part of the adhering acetic acid was driven off. The brittle substance (*B*) was now left in contact with cold alcohol (95 per cent.), which caused it to become superficially white and opaque, part dissolved, and gradually a white, crystalline mass separated, which was collected and washed with cold alcohol. This mass, which weighed 21 grams, was found to consist of unaltered hexa-acetate chlorinated derivatives and of the acetates of the new

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* As the presence even of small quantities of water appears to affect the reaction it was found advisable to employ Kahlbaum's 100 per cent. acetic acid.

*iso*inositol. When dissolved in a large quantity of boiling alcohol the greater part crystallised out on cooling, and by repeated solution of this part in just sufficient alcohol to leave some of the substance undissolved, the unaltered hexa-acetate which formed the greater part of the 21 grams was separated from the more sparingly soluble residue. The latter was recrystallised first from alcohol and then from glacial acetic acid (*a*), and finally once more from alcohol (*b*); it was then pure, and consisted of α-inositolchlorohydrin penta-acetate, $C_6H_6Cl(O{\cdot}CO{\cdot}CH_3)_5$, as the following analyses show:

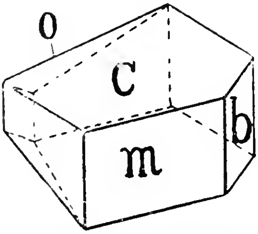
I. Crystallised from acetic acid (*a*):
0·1247 gave 0·2146 CO_2 and 0·0597 H_2O. C = 46·9; H = 5·3.
0·1105 „ 0·1909 CO_2 „ 0·0521 H_2O. C = 47·1; H = 5·2.
0·1593 „ 0·0566 AgCl. Cl = 8·8.

II. Recrystallised from alcohol (*b*):
0·126 gave 0·2117 CO_2 and 0·0564 H_2O. C = 47·1; H = 5·1.
0·1723 „ 0·0623 AgCl. Cl = 8·9.

$C_{16}H_{21}O_{10}Cl$ requires C = 47·0; H = 5·1; Cl = 8·7 per cent.

α-Inositolchlorohydrin penta-acetate melts at 246—247°, and is practically insoluble in water, but it dissolves in benzene, toluene, chloroform, or acetone, less readily in alcohol, and more readily in glacial acetic acid.

FIG 2.



Inositolchlorohydrin penta-acetate. α-Modification.

Crystallographic Measurements.

The crystals from alcohol attained a size of 5 mm., but the character of the faces left much to be desired, so that the accuracy of the crystallographic determination is not so high as with the other substances described in this paper:

System: Monoclinic.

Ratios of the axes: $a:b:c = 0{\cdot}7499:1:0{\cdot}4413$; $\beta = 108°31'$.

Forms: $c - \{001\}$, $m - \{110\}$, $b - \{010\}$, and $o - \{\bar{1}21\}$. The habit was tabular parallel to $c - \{001\}$, and *m* and *b* were about equally well developed; the prism faces were always marked by striations parallel to the prism edge (Fig. 2). It is significant that the form *o* was solely developed at the one end of the axis-*b*, which seems to point to the symmetry being that of the enantiomorphous class of the monoclinic system.

The measurement was effected by adjusting the face $b - (010)$ in the polar position on the two-circle goniometer, and the above constants were calculated from the following measured angles:

	No.	Mean.
$b : m = 010 : \underline{11}0$	6	54°35′
$b : o = 010 : \bar{1}\bar{2}1$	2	49 40½
$[bm] : [bo]$	2	105 55

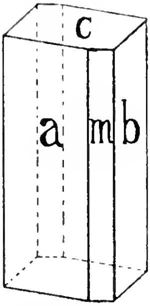
Cleavage: parallel to $b - \{010\}$ very good.

Optics: extinction on b is inclined at an angle of 27° with the prism edge.

D_4^{17} 1·370. Mol. vol. = 298·3.

The alcoholic mother liquors of this substance and those from the recrystallisation of the recovered hexa-acetate having been freed as far as possible from these sparingly soluble substances by systematic concentration, were united with the cold alcoholic extract of (B), and further considerably concentrated, when a substance gradually separated in small, indistinct crystals. This was found to be a mixture, and its separation into its constituents proved to be a very laborious task; but this was finally accomplished by careful fractional crystallisation from 80 per cent. alcohol. As the crystallisation proceeded, the form of the crystals became more distinct, and it thus became possible to separate the different crystals mechanically.

FIG. 3.



Inositolchlorohydrin penta-acetate. β-Modification.

In this way three distinct substances were isolated, and, after repeated recrystallisation, each was obtained pure and in sufficient quantity for analysis and characterisation. Two of these proved to be isomeric modifications of the α-inositolchlorohydrin penta-acetate already described above, and the first, which I propose to call *β-inositolchlorohydrin penta-acetate*, melts at 109—110°:

0·1113 gave 0·1909 CO_2 and 0·0502 H_2O. C = 46·8; H = 5·0.
0·1111 „ 0·1918 CO_2 „ 0·0530 H_2O. C = 47·1; H = 5·3.
0·2042 „ 0·0709 AgCl. Cl = 8·8.
$C_{16}H_{21}O_{10}Cl$ requires C = 47·0; H = 5·1; Cl = 8·7 per cent.

Crystallographic Measurements.

System: Triclinic.

Ratio of the axes: $a : b : c = 0·5451 : 1 :$? ; $\alpha = 95°49'$; $\beta = 98°36'$; $\gamma = 85°39'$.

Forms: $b - \{010\}$, $a - \{100\}$, $m - \{110\}$, and $c - \{001\}$. The habit of the crystals is shown in Fig. 3. Several attempts were made with a view to obtaining crystals with a more abundant form-development, but without success; as a result of this the ratio $c : b$ was indeterminate. The above constants were calculated from the following measured angles, each being the mean of four readings:

	ϕ.	ρ.
b = 010	0° 0′	90° 0′
m = 110	64 18	—
a = 100	93 33	—
c = 001	58 31	10 4

Cleavage: perfect parallel to $b - \{010\}$.

Optics: extinction on b is inclined 38°, and on a 29°, with the prism edge. In convergent light an optic axis is visible through b.

D_4^{17} 1·350. Mol. vol. = 302·7.

The second substance—*γ-inositolchlorohydrin penta-acetate*—crystallises in small, white, rather indistinct crystals, and melts sharply at 118°:

0·1106 gave 0·1908 CO_2 and 0·0520 H_2O. C = 47·0; H = 5·2.
0·1210 „ 0·2091 CO_2 „ 0·0562 H_2O. C = 47·1; H = 5·2.
0·2325 „ 0·0813 AgCl. Cl = 8·7.
$C_{16}H_{21}O_{10}Cl$ requires C = 47·0; H = 5·1; Cl = 8·7 per cent.

The third substance which was isolated melts at 145°, and gave on analysis results which prove that it is *inositolchlorohydrin triacetate*, $C_6H_6Cl(OH)_2(O{\cdot}CO{\cdot}CH_3)_3$, a substance which it may be assumed has been formed by the partial hydrolysis of one of the penta-acetates described above:

0·0991 gave 0·1646 CO_2 and 0·0467 H_2O. C = 45·2; H = 5·2.
0·1101 „ 0·1810 CO_2 „ 0·0521 H_2O. C = 44·8; H = 5·2.
0·0831 „ 0·0384 AgCl. Cl = 11·4.
$C_{12}H_{17}O_8Cl$ requires C = 44·4; H = 5·2; Cl = 10·6 per cent.

During the course of the examination of the aqueous extract (p. 2394) of the crude product of the action of the acetic acid solution of hydrogen chloride on inositol hexa-acetate, a fourth substance was repeatedly observed among the various crystallisations, which had the appearance of slender, acicular crystals, and this was mechanically separated and then recrystallised from dilute alcohol. This substance is *inositolchlorohydrin*, the crystals of which contain two molecules of water of crystallisation, and the substance, after drying at 110°, melts at 180—185°:

0·3533 * lost 0·0524 H_2O at 110°. H_2O = 14·9.
0·1372 gave 0·1542 CO_2 and 0·0825 H_2O. C = 30·7; H = 6·7.
0·1253 „ 0·0766 AgCl. Cl = 15·1.
$C_6H_{11}O_5Cl + 2H_2O$ requires H_2O = 15·3; C = 30·7; H = 6·4;
Cl = 15·1 per cent.

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* Air-dried.

After being dried at 110°, analysis gave the following result:

0·1139 gave 0·1497 CO_2 and 0·0541 H_2O. C = 35·9; H = 5·3.
0·1463 „ 0·1045 AgCl. Cl = 17·7.
$C_6H_{11}O_5Cl$ requires C = 36·2; H = 5·5; Cl = 17·9 per cent.

The corresponding bromohydrin not having been observed during the investigation of the action of hydrogen bromide on inositol hexa-acetate (Trans., 1907, **91**, 1782), search was now made for it in the amorphous residues (*loc. cit.*, p. 1790) from this operation, and, guided by the properties of the chlorohydrin, it was ultimately discovered and isolated in a pure condition.

Inositolbromohydrin has properties which are very similar to those of the chlorohydrin; it occurs in flat, prismatic crystals, which melt at 170—175°, and turn black at 180°. It is readily soluble in warm water, and also in boiling absolute alcohol, and separates from the latter, on cooling, in tufted crystals, which, however, do not change at 100°, and are presumably anhydrous:

0·4389 * lost 0·0322 H_2O at 110°. H_2O = 7·3.
0·4072 „ 0·0256 H_2O „ 110°. H_2O = 6·9.
$C_6H_{11}O_5Br + H_2O$ requires H_2O = 6·9 per cent.

0·1131 † gave 0·1247 CO_2 and 0·0479 H_2O. C = 30·0; H = 4·7.
0·1493 „ 0·1048 AgBr. Br = 29·8.
$C_6H_{11}O_5Br$ requires C = 29·7; H = 4·5; Br = 30·6 per cent.

Although the chlorinated derivatives just described are the only crystalline substances which could be obtained from the part of the product soluble in alcohol, the alcoholic mother liquors from all these substances still contained a considerable portion of the product of the reaction, and this was left, on evaporation, in the form of a colourless, transparent, brittle, glassy mass, readily fusible under hot water to a heavy liquid, but only sparingly soluble therein. Its origin and properties suggested at once that it was probably similar to the brittle, glassy substance which had been previously observed among the products of the action of hydrogen iodide on inositol hexa-acetate, and which was shown to contain the acetyl derivatives of two new isomerides, namely, *iso*inositol and ψ-inositol (compare p. 2393).

This view proved to be correct since, on hydrolysis with hydrochloric acid, these new substances were isolated.

It remains now to refer back to the part *A* of the original product readily soluble in water (p. 2394). After evaporation of the solution it formed an amorphous substance, which, on further examination, was found to consist of a mixture of the new isomerides with a chlorinated compound. The latter, on account of its unfavour-

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* Air-dried. † Dried at 110°.

able properties, could not be separated or obtained in a pure and definite condition; but there is valid reason for assuming that it is an acetylchlorohydrin or chlorohydrin of ψ-inositol. The presence of this chlorinated derivative presented an unexpected difficulty to the further progress in the working-up of this part of the product until later on when the drastic means of destroying it had become available.

Action of Hydrogen Chloride on Inositol.

Meanwhile, experiments had established the fact that these new isomerides could be more readily obtained by acting on anhydrous inositol itself with an acetic acid solution of hydrogen chloride at an elevated temperature.

Under these conditions none of the crystallised chlorinated derivatives are formed, and after sufficiently prolonged heating the whole of the inositol is converted into the new isomerides and their acetates; but also in this case, associated with the acetylchlorohydrin mentioned above. This led to the elaboration of the following method, which offers considerable advantages, and served for the preparation of the material for a more extended investigation of *iso*inositol and ψ-inositol.

Inositol previously dried at 120°, in quantities of 10 grams, was heated in sealed tubes at 160° for sixty hours with glacial acetic acid (Kahlbaum's 100 per cent.), saturated with hydrogen chloride, and the pale brown product distilled under diminished pressure and treated otherwise in the manner already described; but the crude product obtained in this case exhibited a marked difference from that resulting in the reaction previously described. It formed a gummy substance readily soluble both in alcohol and water, and on examination was found to contain *iso*inositol and ψ-inositol, mainly in the form of acetates which were amorphous and soluble in all proportion in alcohol and water, thus differing in this respect from the acetates hitherto noticed. Besides these it contained also a considerable quantity of the chlorinated derivative, ψ-inositolchlorohydrin, mentioned above. Accordingly, the product was now submitted to the action of a boiling solution of barium hydroxide which effected the hydrolysis of the acetates, and, at the same time, converted the ψ-inositolchlorohydrin into a brown colouring matter, which could be readily removed, partly by filtration and partly by treatment with animal charcoal. The filtrate, after being freed from barium, left on evaporation a residue which now resembled the substance obtained by a similar procedure on former occasions. The gummy, semi-transparent mass, which had been dried at 125°

and broken into pieces, was now covered with cold 60 per cent. alcohol and left to remain. This caused the surface to become white and then rough by the appearance of minute, white crystals, and in the course of a few days the pieces had become white throughout, and quite friable masses which were crushed and washed with 60 per cent. alcohol; thus the inositol was separated in a condition approaching purity. It must, however, be observed here that the complete separation from the still adhering ψ-inositol could only be effected by careful precipitation of the aqueous solution with concentrated alcohol, and taking care to avoid an excess of alcohol which would throw down the ψ-inositol as well; but even then the precipitation had to be repeated several times.

Finally, the *iso*inositol is crystallised from hot 50 per cent. alcohol or from water, and it may be remarked here that the best developed crystals are produced by evaporating the aqueous solution at a temperature approaching 100°. If an aqueous solution is allowed to evaporate and crystallise at the ordinary temperature, minute, white crystals of a hydrate are formed, which resemble suspended china-clay, and, when first noticed, were supposed to be a new substance. Being less soluble in water, they could be fairly well separated from the anhydrous crystals mixed with it, but on dissolving it and evaporating the solution, well-defined characteristic crystals of the anhydrous *iso*inositol separated, but none of the white hydrate.

*iso*Inositol crystallises in well-developed, transparent, and lustrous crystals. It is readily soluble in water, and it was found that 100 c.c. of water at 18° dissolve 25·12 grams of *iso*inositol and 100 c.c. of water at 100° dissolve 43·22. A tendency, too, of forming supersaturated solution in the cold was frequently noticed. It is insoluble in ether, benzene, or chloroform, practically insoluble in absolute alcohol, but soluble to a considerable extent in boiling 50 per cent. alcohol, from which it almost completely separates in crystals on cooling. The solution in water exhibited no indication of optical activity, and it has but a very faint, sweet taste. The aqueous solution gives a copious, slimy precipitate with basic lead acetate, and a weak alcoholic solution yields, on the addition of a methyl-alcoholic solution of barium hydroxide, a white precipitate of the barium derivative, which is soluble in water. When it is heated with nitric acid, evaporated carefully to dryness, the residue dissolved in water, mixed with calcium chloride, and again evaporated, the fine red colour of calcium rhodizonate is produced, which is the characteristic inositol reaction of Scherer.

When heated it begins to turn brown at 225°, and melts and evolves gas at 246—250°.

Crystallographic Measurements.

System: Monoclinic.

Ratios of the axes: $a:b:c = 1{\cdot}2390:1:1{\cdot}0500$; $\beta = 92°33'$.

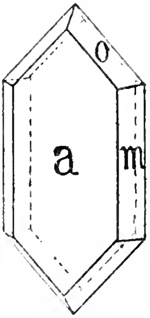
Forms: $a-\{100\}$, $m-\{110\}$, and $o-\{111\}$. The habit is tabular parallel to $a-\{100\}$, and the crystals are almost invariably twinned with a as twin plane, as shown in Fig. 4. As a result of the twinning the crystals simulate orthorhombic symmetry, and it is only by means of an optical examination that the true symmetry is revealed. Only one crystal was found untwinned out of about twenty examined. Following are the mean measured and calculated angles:

		Mean measured.		Calculated.	
	No.	ϕ.	ρ.	ϕ.	ρ.
$m = 110$	8	*38°55½′	90° 0′	—	—
$a = 100$	3	90 0	—	—	—
$o = 111$	4	*40 22	*54 2	—	—
o twin	2	319 51	53 42	319°33′	54°2′

Cleavage: none observed.

Optics: The twin crystals lying on the tabular face do not wholly extinguish, but the position of maximum darkness is parallel to the trace of the symmetry plane. In convergent light very remarkable interference figures were obtained, proving that the axial plane is the plane of symmetry. By cutting a crystal parallel to the plane of symmetry (010) it was found that the acute and obtuse bisectrices approximately bisect the angle-β. The axial angle is medium, the birefringence strong.

FIG. 4.



*iso*Inositol.

D_4^{18} 1·684. Mol. vol. = 106·9.

*iso*Inositol in well-developed, lustrous crystals, which remained quite unaltered at a temperature of 120°, gave the following results on analysis:

0·1101 gave 0·1621 CO_2 and 0·0691 H_2O. C = 40·2; H = 6·9.

$C_6H_{12}O_6$ requires C = 40·0; H = 6·7 per cent.

Subsequently a crystallisation of somewhat different appearance and less definite was obtained, which, after drying over sulphuric acid, gave on analysis:

0·1099 gave 0·1548 CO_2 and 0·0669 H_2O. C = 38·4; H = 6·8.

$C_6H_{12}O_6 + \frac{1}{2}H_2O$ requires C = 38·1; H = 6·9 per cent.

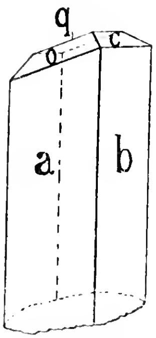
When this hydrated specimen was dried at 100° it gave on analysis:

0·1096 gave 0·1603 CO_2 and 0·0671 H_2O. C = 39·8; H = 6·7.

iso*Inositol Hexa-acetate*, $C_6H_6(O{\cdot}CO{\cdot}CH_3)_6$.

This compound has already been noticed in the course of the investigation of the products of the action of hydrogen iodide on inositol hexa-acetate, when it was prepared for the purpose of effecting the elimination of some inositol, which contaminated the resulting *iso*inositol; but on that occasion a closer examination of its properties was not made. The following experiments were carried out with the pure substance. The acetylation of *iso*inositol by means of acetic anhydride and a trace of zinc chloride takes place with great ease, and, once started, proceeds without further application of heat. On treatment of the product in the usual way with water, a heavy, oily liquid results, which soon becomes a crystalline solid, and this, on being dissolved in warm 80 per cent. alcohol, separates on cooling in massive crystals, which, under favourable conditions, attain a length of several centimetres. They are quite different in appearance from the crystals of inositol hexa-acetate. A very concentrated alcoholic solution, on the other hand, on cooling, becomes milky, and deposits globules which gradually solidify, and then the solution becomes filled with slender crystals. This acetate is soluble to some extent in water, and the concentrated hot solution on cooling in this case also becomes first milky and then deposits crystals. One hundred c.c. of a boiling saturated solution contain 0·89 per cent., and 100 c.c. of the mother liquor at 18° contain only 0·14 per cent. Although it fuses in the pure state at 112° it shows the remarkable behaviour of melting to a heavy oil when boiled with water. It is readily hydrolysed by barium hydroxide solution and hot concentrated hydrochloric acid:

FIG. 5.



iso*Inositol hexa-acetate.*

0·1643 gave 0·3002 CO_2 and 0·0862 H_2O. C = 49·8; H = 5·8.

$C_{18}H_{24}O_{12}$ requires C = 50·0; H = 5·6 per cent.

Crystallographic Measurements.

System: Triclinic.

Ratios of the axes: $a:b:c = 1{\cdot}3705:1:0{\cdot}7537$; $\alpha = 111°52'$, $\beta = 87°4'$, $\gamma = 112°3'$.

Forms: $b - \{010\}$, $a - \{100\}$, $c - \{001\}$, $o - \{111\}$, and $q - \{0\bar{1}1\}$. The habit was prismatic, and the three terminal faces were about equally well developed. A typical crystal is shown in Fig. 5. Following are the results obtained by measurement of five crystals on the two-circle goniometer:

	Mean observed.		Calculated.	
	ϕ.	ρ.	ϕ.	ρ.
$b=010$	0° 0′	90° 0′	—	—
$a=100$	*67 23	90 0	—	—
$o=1\bar{1}1$	*115 24	*28 56	—	—
$c=001$	*352 56	*22 37	—	—
$q=0\bar{1}1$	186 15	25 5	186°16′	25°8′

Cleavage: imperfect parallel to $b-\{010\}$ and $q-\{0\bar{1}1\}$.

Optics: extinction on $b-\{010\}$ makes an angle of 19°, on $a-\{100\}$ an angle of 29° with the prism edge. In convergent light an optic axis is visible through b, central; whilst through a there is no axis visible. The birefringence is medium.

D_4^{19} 1·266. Mol. vol. $=$ 341·4.

iso*Inositol Benzoate.*

While searching for a ready process for effecting the separation of the two new isomerides *iso*inositol and ψ-inositol, it appeared likely that the preparation of the benzoates of these compounds might lead to the desired result. An experiment made with the mixture of the two as resulting in the process described (p. 2399) was, however, only successful in so far that *iso*inositol benzoate could be separated in a pure state, whilst ψ-inositol benzoate, being amorphous and differing but little in solubility, retained to the last more or less of the former.

For the further examination some of the *iso*inositol benzoate was subsequently prepared from pure crystallised *iso*inositol in the following manner. Two grams of finely powdered anhydrous *iso*inositol were gently heated with 15 c.c. of benzoyl chloride, when hydrogen chloride was evolved and the substance gradually dissolved. After raising the temperature by degrees and continuing the operation for six hours the disengagement of hydrogen chloride ceased. On cooling, the product formed a perfectly clear semi-liquid substance, which was dissolved in pure benzene and shaken repeatedly with a dilute solution of sodium carbonate. The benzene solution on evaporation left *iso*inositol benzoate in the form of a white, crystalline powder.

For further purification it was dissolved in boiling 99 per cent. alcohol, and on cooling it separated in voluminous, minute, acicular crystals. In order to free it from a slight admixture of an amorphous compound, which appears to be a lower benzoate, it was dissolved in a just sufficient quantity of hot acetone, from which solvent it separated on cooling in crystals of considerable size containing acetone of crystallisation, which, however, is given off on exposure to the air, leaving the benzoate in the form of a white powder. However, on adding to the hot acetone solution one-fifth of its volume of hot water the solution on cooling deposits brilliant and well-formed crystals, which retain their lustre when dried.

On recrystallisation once more from alcohol some aggregations of silky tufts made their appearance amongst the massive and brilliant crystals which formed the main part of the product.

The latter, when finally separated, melted at 213°, and an analysis gave the following result:

0·1769 gave 0·4438 CO_2 and 0·0755 H_2O. C=68·4; H=4·7.

$C_{34}H_{28}O_{10}$ requires C=68·4; H=4·7 per cent.

This iso*inositol tetrabenzoate*, $C_6H_6(OH)_2(OBz)_4$, is most readily soluble in acetone, less so in benzene or ether; in alcohol (90 per cent.) it is but sparingly soluble, and 100 c.c. at boiling temperature dissolve 1·78 grams, and 100 c.c. at 18° only retain 0·09 gram in solution.

The above-mentioned silky tufts melted at 208—211°, and on analysis gave:

0·1582 gave 0·3986 CO_2 and 0·0659 H_2O. C=68·7; H=4·6,

and appear, therefore, to be merely a different form of the tetrabenzoate; but on account of want of material this point must be left in abeyance for the present.

ψ-Inositol.

Although the investigation of the products of the action of hydrogen iodide on inositol hexa-acetate (p. 2391) had to a certain extent revealed the individuality of this substance, it was only when the hydrochloric acid reaction furnished more readily a supply of material for examination that its true chemical nature could be ascertained.

The difficulty which confronts the final isolation of *iso*inositol is caused by the close resemblance the two substances bear to each other, especially in their solubility. This is accentuated by the solvent action which ψ-inositol has on *iso*inositol, thereby impeding its crystallisation and causing the gummy condition referred to.

It follows from what has been said about the final process in the isolation of the inositol (p. 2400) that ψ-inositol, being somewhat more soluble, accumulates in the mother liquor, but carrying with it some of the former. After various ineffectual trials, the following plan for separating this admixture was adopted. The mother liquor was concentrated on the water-bath to the consistence of a thin syrup, and some alcohol added, which caused the separation of ψ-inositol as a heavy, viscid, oily liquid, from which, on being kept for some time in the ice-box, the dissolved *iso*inositol gradually crystallised out. Eventually the ψ-inositol was obtained as a colourless, transparent, brittle gum, which is very hygroscopic and soluble in all proportions in water. It is only very sparingly soluble in concentrated alcohol; in 50 per cent. alcohol it dissolves freely, and by the addition of concentrated alcohol to such a solution a white, curdy precipitate forms and separates as a heavy, oily liquid, which remains unaltered, and does not solidify even when kept for a long time at a low temperature. If, however, the supernatant liquid is decanted and replaced by fresh 99 per cent. alcohol, the oil gradually becomes solid, and on one particular occasion, after being kept for some months, it was converted into a microcrystalline mass resembling grape sugar.

An aqueous solution of ψ-inositol is precipitated by basic lead acetate, and an alcoholic solution by that of methyl-alcoholic barium hydroxide and alcoholic solution of cuprammonium, and in this respect it behaves exactly like inositol and *iso*inositol.

ψ-Inositol gives also Scherer's rhodizonate reaction. When treated with acetic anhydride in the usual manner, the acetate is produced; but on account of the substance caking together, the reaction is not very energetic. The product is an amorphous solid, readily fusible and sparingly soluble in hot water, but very readily soluble in alcohol, ether, benzene, or acetone. It seems to have a particular affinity for acetic acid, which readily dissolves it, and is only with difficulty separated.

ψ-Inositol readily dissolves in cold concentrated nitric acid (D 1·4), and on addition of fuming sulphuric acid the nitrate is precipitated. When purified it forms a colourless, amorphous substance, which on being heated, first melts and boils and then explodes with moderate energy. It appears to undergo spontaneous decomposition when kept for some time.

For the purpose of analysis, the powdered ψ-inositol contained in a platinum boat was heated at 100° in a desiccator over phosphoric oxide for several hours, and then quickly weighed and transferred to the combustion tube:

0·1588 gave 0·2313 CO_2 and 0·0980 H_2O. C = 39·7; H = 6·8.
0·1601 „ 0·2321 CO_2 „ 0·0995 H_2O. C = 39·5; H = 6·9.
$C_6H_{12}O_6$ requires C = 40·0; H = 6·3 per cent.

Action of Hydrogen Bromide on Scyllitol Hexa-acetate.

In a former communication on cocosite (cocositol, scyllitol) (Trans., 1907, **91**, 1779) I mentioned that by the action of a glacial acetic acid solution of hydrogen bromide on cocosite hexa-acetate results were obtained, which exhibited a close analogy to those obtained with inositol hexa-acetate. Further investigation led to the unexpected and interesting result that the products thus obtained are actually identical with those obtained from inositol hexa-acetate, and the significant fact will be noticed that in this case also the crude product of the reaction consists of a complex mixture of substances from which, in the course of the work, one after the other of the so characteristic and well-crystallised brominated derivatives could be isolated which had been previously obtained from inositol hexa-acetate. There is, however, a very marked difference in the facility with which the hydrogen bromide acts on these two acetates. Whilst in the case of inositol acetate the reaction sets in at about 100°, scyllitol acetate requires continued heating for several days at a temperature of 145—150°.

Scyllitol hexa-acetate (10 grams) was heated in a sealed tube with 50 c.c. of a saturated solution of hydrogen bromide in glacial acetic acid for some days in the boiling-water bath; but as no appreciable action had taken place, the operation was continued for some days at 110—120°, and as the reaction had still not proceeded very far, the tube was finally heated for several days at 145—150°. The contents were filtered through an asbestos filter in order to separate some unaltered acetate, which amounted to 1·7 per cent. of the acetate employed. The filtrate was distilled under diminished pressure to remove the hydrogen bromide and acetic acid, and the brown, semi-solid residue was then digested with water. The part insoluble in water became, on cooling, a hard, crystalline mass, which dissolved almost entirely in much boiling alcohol, leaving a small, crystalline residue, which, after further precipitation, was obtained in minute crystals which melted at 240°, and proved to be identical with inositolbromohydrin penta-acetate (monobromoinositol penta-acetate) (Trans., 1907, **91**, 1783). The hot alcoholic solution deposited, on cooling, indistinct crystals, which on recrystallisation assumed more and more the characteristic appearance of the scaly modification of dibromoinositol tetra-acetate:

0·2167 gave 0·1717 AgBr. Br = 33·7.

$C_{14}H_{18}O_8Br_2$ requires Br = 33·7 per cent.

That this substance is identical with the scaly dibromo-derivative obtained in a corresponding manner from inositol hexa-acetate was proved, not only by the identity of the melting point (235°), but also by the fact that the mixture of the two specimens also melted at this temperature. From the mother liquor of this substance the massive modification of dibromoinositol tetra-acetate previously described (*loc. cit.*, p. 1784) and melting at 140° was isolated in small quantity, but comparatively large crystals of its characteristic form.

The aqueous solution obtained by extracting the crude product with hot water was repeatedly evaporated with water to remove the remainder of the acetic acid, during which operation the characteristic odour of bromobenzene was noticed, and, from the residue, characteristic, well-developed crystals of inositoldibromohydrin melting at 210° were obtained.

Subsequently from the remaining aqueous mother liquor a small quantity of inositolbromohydrin melting at 170—175°, *iso*inositol and ψ-inositol were also isolated.

These results prove that the products of the action of an acetic acid solution of hydrogen bromide on scyllitol hexa-acetate are identical with those obtained when inositol hexa-acetate is subjected to the same treatment.

The Action of Hydrogen Chloride on Scyllitol.

The action of hydrogen bromide on scyllitol hexa-acetate having led to the interesting result that the derivatives thus obtained are in all respects identical with those which are produced by the same reagent when acting on inositol hexa-acetate, it appeared more than probable that scyllitol, when submitted to the action of hydrogen chloride, would yield the same derivatives as inositol gave when heated with a glacial acetic acid solution of hydrogen chloride.

It was a matter of interest to determine whether this is actually the case, and as the results obtained in more recent experiments with inositol itself had shown that the employment of the acetate offers no advantage, it was decided to use scyllitol as such in the present case.

Preliminary experiments showed that scyllitol is much less readily attacked by an acetic acid solution of hydrogen chloride than inositol, and the reaction proceeds very slowly at 140°, and even after heating for several days at 160° a considerable proportion of the scyllitol remained unchanged.

For this investigation, scyllitol finely powdered was heated in quantities of 5 grams at 160° for seventy hours in sealed tubes with 50 c.c. of a saturated solution of hydrogen chloride in glacial acetic acid. The contents of the tubes were distilled under diminished pressure in order to remove hydrogen chloride and acetic acid, and the dark syrupy residue allowed to remain, when it gradually deposited crystals of unaltered scyllitol. The whole was stirred with water, filtered, and the less soluble part digested with hot water, which dissolved most of it, but left a dark-coloured residue, from which hot alcohol extracted a small quantity of a crystallised substance, which on examination was found to be a mixture of scyllitol hexa-acetate with another scyllitol acetate of a much lower melting point and more readily soluble than the former.* The part insoluble in alcohol was a dark purplish-black powder, soluble in alkali with a reddish-violet colour, and seemed to be identical or similar to that noticed during the investigation of the action of hydrogen iodide on inositol hexa-acetate (p. 2393).

The above-mentioned solution of the less soluble portion of the crude product in hot water yielded, on concentration, unaltered scyllitol amounting to more than half of that which had been employed. From the mother liquor of this, added to the above-mentioned cold aqueous extract of the more readily soluble portion of the crude product, after treatment with animal charcoal and repeated evaporation with water, a syrup was obtained which finally became a semi-crystalline mass. This, when stirred with cold alcohol, left a crystalline substance, which separated from hot dilute alcohol (60 per cent.) in voluminous, silky tufts, and after being freed from traces of scyllitol by repeated recrystallisation a substance was obtained which contained chlorine and water of crystallisation and generally resembled inositolchlorohydrin (m. p. 145°, compare p. 2397), but had the much higher melting point of about 200°, at which temperature it began to decompose:

0·1372 gave 0·1542 CO_2 and 0·0825 H_2O. C = 30·7; H = 6·7.
0·1253 „ 0·0766 AgCl. Cl = 15·1.
$C_6H_{11}O_5Cl + 2H_2O$ requires C = 30·7; H = 6·4; Cl = 15·1 per cent.

Another specimen of this substance, after being dried at 100°, gave the following results:

0·1201 gave 0·1592 CO_2 and 0·0604 H_2O. C = 36·2; H = 5·5.
0·1559 „ 0·1122 AgCl. Cl = 17·8.
$C_6H_{11}O_5Cl$ requires C = 36·3; H = 5·5; Cl = 17·8 per cent.

There seems, therefore, no doubt that this substance is scyllitolchlorohydrin. As indicated by its preparation, it is readily soluble both in water and in dilute alcohol, but in absolute alcohol, benzene, or acetone it is practically insoluble.

The remaining mother liquor contained another substance, which

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* Special experiments showed that the lower scyllitol acetates are also produced when scyllitol hexa-acetate is heated in absolute alcohol. Scyllitol hexa-acetate, in quantities of 3 grams, was heated with 30 c.c. of absolute alcohol in sealed tubes for 50 hours at 160°. Ethyl acetate and acetic acid were eliminated, and a mixture of different acetates was obtained, from which several could be isolated in a sufficiently pure state to show their identity with those described above. There was one, however, that had not been isolated from the product of the hydrogen chloride action and which was more soluble, both in water and alcohol, and, in this respect, resembled the inositol triacetate obtained by the action of alcohol on inositol hexa-acetate (p. 2409). In one experiment, when the heating of the tube was continued for eighty hours, the acetate was completely decomposed, and nothing but the scyllitol remained.

appeared in the form of minute crystals, and otherwise different from the one just described, but could not be obtained in a sufficiently pure state for analysis. From the fact that on boiling it with hydrochloric acid it yielded scyllitol and acetic acid, it is evident that it is an intermediate acetate of scyllitol.

For further treatment the mother liquor was now evaporated, and the concentrated liquid mixed with ether, which produced a copious, white, viscid precipitate. The ether on evaporation left a viscid residue, which contained a chlorinated compound apparently identical with the one obtained by this same reaction on inositol (p. 2399), and also the acetates of *iso*inositol and ψ-inositol, and a minute quantity of some scyllitol acetate. It was accordingly submitted to the same treatment with barium hydroxide as described (p. 2399), and the *iso*inositol and ψ-inositol thus isolated. The ether precipitate consisted of free *iso*inositol and ψ-inositol. It is thus shown that in this reaction a part of scyllitol is transformed into three different acetates and its chlorohydrin, whilst another part is converted into *iso*inositol and ψ-inositol and their acetates.

Inositol Triacetate.

In the course of this investigation is became evident that during the action of the halogen hydrides on inositol hexa-acetate also a more or less complete breaking down of the acetate is involved, which would give rise to the formation of lower acetates. It is stated that a penta-acetate (m. p. 216°) and a triacetate have been noticed, both said to be crystallised substances (Fick, *Chem. Centr.*, 1887, 452). These were accordingly sought for amongst the crystallised substances under investigation, but without their presence being detected. Nevertheless, there were indications that some such lower acetates were actually contained in the more soluble part of the residual product which could not be crystallised. It was of interest, therefore, to devise some method for preparing such lower acetates in order to get an idea as to their characteristic properties, and it was found that by heating the hexa-acetate with concentrated alcohol this object could be obtained.

Ten grams of inositol hexa-acetate with 80 c.c. of alcohol (99 per cent.) were sealed up in a tube and heated for six hours at 130°, when, after cooling, it was found that a large quantity of the substance had remained undissolved. The heating was then continued at intervals, and the temperature having been finally raised to 180° no more crystals appeared after cooling. The contents of the tube left, on distilling, a colourless, viscid residue, which on being mixed with water caused the separation of a crystallised substance. This proved to be pure unaltered hexa-acetate, and amounted to 0·75 gram. The presence of ethyl acetate was noticed in the distillate, and there was also some free acetic acid present in the residue. The solution was evaporated, and the residue kept for some time at a temperature of 125° in a melted state. The product on being placed in cold acetone mostly dissolved, but left a small quantity of an amorphous compound, which was not further examined.

All attempts to obtain any crystallised substance from this product failed, and there were no means for ascertaining whether this substance was a simple or complex compound. It was finally obtained as a colourless, transparent, brittle, gummy substance, which cracked in all directions. It is very hygroscopic, and soluble in all proportions in water or alcohol, sparingly soluble in ether, a little more so in benzene, but readily soluble in acetone. It retains these solvents with great tenacity, and had, therefore, to be kept at a temperature approaching 120° when being prepared for analysis:

0·1058 gave 0·1834 CO_2 and 0·0606 H_2O. C=47·0; H=6·2.
$C_6H_9O_3(O{\cdot}CO{\cdot}CH_3)_3$ requires C=47·1; H=5·9 per cent.

0·526, hydrolysed with methyl-alcoholic barium hydroxide, gave 0·579 $BaSO_4$, and 0·296 anhydrous inositol; these numbers approach nearest to inositol triacetate, which requires 0·6017 $BaSO_4$ and 0·3167 inositol.

It may be added here that experiments carried out with the view of effecting this limited hydrolysis by means of water have not given the desired results, for it has been found that at 130° no perceptible action takes place, but when the temperature was raised to 160° the hydrolysis was complete, and the inositol was entirely liberated.

In conclusion, I beg to offer my thanks to the managers of the Davy-Faraday Laboratory for having afforded me the opportunity of carrying out these investigations.

Davy-Faraday Laboratory,
Royal Institution.

CCLII.—*The Constituents of Taraxacum Root.*

By FREDERICK BELDING POWER and HENRY BROWNING, jun.

THE root of the common dandelion (*Taraxacum officinale*, Wiggers) appears to have been employed medicinally for several centuries, and it still maintains a place in the more important national Pharmacopœias. It is therefore somewhat remarkable that up to the present time so little of a definite nature should be known respecting its constituents, for, apart from the observed presence of inulin—which is common to the family of *Compositæ*—lævulin, and such ordinary constituents of plants as sugar, resin, and mucilage, no well-characterised compound has hitherto been isolated from this root.

Polex (*Arch. Pharm.*, 1839, **19**, 50) has stated that on boiling the milky juice of taraxacum with water, filtering and concentrating the liquid, a crystalline substance was obtained which was sparingly soluble in cold water, but readily so in boiling water, alcohol, or ether, and possessed an agreeably bitter, somewhat acrid taste. This substance was termed "taraxacin," but no analysis, melting point, or other characters were recorded which would serve for its identification. It was also noted by Polex (*loc. cit.*) that the resinous and albuminous material which separated on heating the milky juice to boiling, when extracted with alcohol, yielded a substance which crystallised in a white, cauliflower-like form.

Kromayer (*Arch. Pharm.*, 1861, **105**, 6) examined the dried milky juice of the plant, for which he proposed the name "leontodonium." From the portion of this which was soluble in water he obtained some crystals mixed with amorphous material, but did not succeed in isolating the so-called "taraxacin." The portion of the dried milky juice which was insoluble in water yielded, on extraction with alcohol, "tasteless, spherical granules," which the author designated as "taraxacerin." An analysis ($C=79{\cdot}44$; $H=12{\cdot}69$ per cent.) was recorded of this substance, but no melting point, and to it the formula $C_{40}H_{80}O_5$ (or the simpler expression $C_8H_{16}O$) has since been assigned.

It is apparent from present knowledge that the so-called "taraxacin" and "taraxacerin" of the above-mentioned authors could not have been pure or homogeneous substances. The statements which have subsequently been recorded in the literature respecting the proportion of "taraxacin" in taraxacum root, with the assumption that it represents a distinct bitter principle, are therefore quite illusory.

L. E. Sayre has more recently contributed a number of papers on the subject of taraxacum (*Proc. Amer. Pharm. Assoc.*, 1893, p. 77; 1894, p. 241; 1895, p. 203; 1896, p. 160; 1897, p. 223; 1898, p. 341), but his investigations do not appear to have resulted in the isolation of any definite constituent of the root.

The question regarding the occurrence of mannitol in taraxacum root was investigated many years ago by T. and H. Smith (*Pharm. J.*, 1849, **8**, 480), who conclusively proved that this compound does not pre-exist therein, but that it is formed when an extract of the root undergoes the so-called mucous or viscous fermentation. Its formation under these conditions would appear to permit of explanation by the fact that taraxacum root contains an abundance of inulin, which, on hydrolysis, is converted into lævulose, and the latter, by the special fermentative process referred to, becomes reduced to mannitol. The above observation has now also been confirmed by the present authors, inasmuch as no trace of mannitol could be isolated directly from the root employed for this research.

While the present investigation was in progress it has been recorded (*Brit. Med. J.*, May 25th, 1912, p. 1181) that the use of taraxacum in cases of cancer has been attended with remarkably beneficial results, and shortly afterwards (*ibid.*, July 13th, 1912, p. 97) attention was directed to the use of choline in the treatment of this disease. Additional interest is imparted to these two quite independent observations, especially when considered conjointly, by the fact that taraxacum root has now been found to contain choline. The various other well-defined compounds which have been isolated are summarised at the end of this paper.

EXPERIMENTAL.

The material employed for this investigation consisted of the best quality of English taraxacum root, which was collected in the autumn of 1911, and kindly supplied to us by Messrs. W. Ransom and Son, of Hitchin.

A small portion (25 grams) of the ground root was treated with Prollius' fluid, and the resulting product tested for an alkaloid with the usual reagents. The reactions obtained were so slight as to indicate the presence of not more than traces of an alkaloidal substance.

Another portion (20 grams) of the ground material was successively extracted in a Soxhlet apparatus with various solvents, and the resulting extracts dried in a water-oven until of constant weight:

Petroleum (b. p. 35—60°)	extracted	0·28	gram	= 1·40	per cent.
Ether	,,	0·06	,,	= 0·30	,,
Chloroform	,,	0·05	,,	= 0·25	,,
Ethyl acetate	,,	0·34	,,	= 1·70	,,
Alcohol	,,	2·33	,,	= 11·65	,,
Water	,,	10·20	,,	= 51·00	,,
Total		13·26	grams	= 66·3	per cent.

In order to ascertain whether an enzyme were present, 200 grams of the air-dried root were extracted with cold water, and to the clear, filtered liquid about twice its volume of alcohol was added. A slight precipitate was thus produced, which, when collected and dried in a vacuum over sulphuric acid, could be reduced to a brown powder. This product, which amounted to 0·85 gram, very slowly hydrolysed amygdalin, and thus possessed some enzymic activity.

For the purpose of a complete examination of the constituents of the root, 22·9 kilograms of the dried, ground material were extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, 7·3 kilograms of a viscid, dark-coloured extract were obtained.

One kilogram of the alcoholic extract, representing about 3·14 kilograms of the root, was examined for sucrose by the following method: The extract was first mixed with water to separate the resin, which was incorporated with the larger portion subsequently obtained, and designated as (*B*). The filtered, aqueous liquid was then treated with an excess of milk of lime, again filtered, and the alkaline filtrate saturated with carbon dioxide. This liquid, after filtration, was evaporated under diminished pressure to the consistency of a syrup, and the latter treated with successive portions of alcohol until a product was finally obtained, which dissolved completely in alcohol of about 85 per cent. strength. The solution of this product, when decolorised with a little animal charcoal and kept for several months, deposited no crystalline substance, and there was therefore no indication of the presence of sucrose.

Distillation of the Extract with Steam. Separation of an Essential Oil.

The entire remaining portion (6·3 kilograms) of the above-mentioned alcoholic extract of the root was mixed with water, and distilled in a current of steam. The distillate was extracted with ether, the ethereal liquid dried, and the solvent removed, when a small amount of a dark yellow essential oil was obtained. This oil had a strong, persistent odour, and gave the colour reaction for furfuraldehyde.

Non-volatile Constituents of the Extract.

After the above-described operation there remained in the distillation flask a dark-coloured aqueous liquid (*A*), together with a quantity of a soft, somewhat oily resin (*B*). The resinous material, the separation of which was attended with considerable difficulty, was finally washed thoroughly with warm water, and the washings added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

The aqueous liquid, after concentration under diminished pressure, was extracted many times with ether. These ethereal liquids were united, the greater portion of the solvent removed, and the residue mixed with about an equal volume of light petroleum (b. p. 35—50°), when a red oil was deposited. On decanting and concentrating the supernatant liquid, and again treating it with light petroleum, further small quantities of red oil were obtained, which were added to the first portion. The mixture of ether and light petroleum was finally evaporated, the residue dissolved in ether, and the ethereal liquid shaken successively with aqueous ammonium carbonate, sodium carbonate, and sodium hydroxide. Each of these alkaline liquids was acidified, extracted with ether, and the solvent evaporated.

Isolation of p-*Hydroxyphenylacetic Acid*, $C_6H_4(OH)\cdot CH_2\cdot CO_2H$.

The product obtained from the above-mentioned ammonium carbonate extract was a dark yellow oil. This was treated with hot water and a little animal charcoal, and the liquid filtered, when, on cooling, a gum-like mass separated, which gradually became crystalline. After recrystallisation from benzene containing a little ethyl acetate, a very small amount (about 0·05 gram) of an acidic substance was obtained, which separated in colourless needles, melting at 144—145°. The above-mentioned red oil, which was deposited by the addition of light petroleum to the concentrated ethereal liquid, was redissolved in ether, and extracted successively with aqueous alkalis, as already described. The ammonium carbonate extract thus obtained, when acidified, yielded a gum-like product, which was esterified. The acid was then regenerated from the ester and crystallised several times from ethyl acetate, when it separated in flat needles melting at 144—146°, and amounted to about 0·4 gram. It was identical with the small portion (0·05 gram) of acid first obtained. By the subsequent extraction of both portions of the original ethereal extract with sodium carbonate and sodium hydroxide respectively, only small amounts of dark-coloured, amorphous products were obtained, from which nothing definite could be isolated.

The above-described acid was dried at 105° and analysed:

0·0632 gave 0·1451 CO_2 and 0·0294 H_2O. C=62·6; H=5·2.
0·0818 „ 0·1894 CO_2 „ 0·0379 H_2O. C=63·1; H=5·1.
0·1009 neutralised 32·5 c.c. $N/50$-KOH. M.W. (monocarboxylic acid)=155.
$C_8H_8O_3$ requires C=63·1; H=5·3 per cent. M.W.=152.

A determination of the molecular weight of the acid by Barger's microscopic method was kindly made for us by Mr. A. J. Ewins, B.Sc., with the following result:

0·048 in 1·196 of absolute alcohol, using α-naphthol as the standard, was between 0·26 and 0·275 mol. Mean M.W.= 150.

The acid was soluble in cold, and more readily in warm, water, as also in alcohol, ether, ethyl acetate, and acetone, but only slightly so in benzene or the higher boiling fractions of petroleum. Its dilute aqueous solution gave no perceptible coloration with ferric chloride. With Millon's reagent it yielded the deep red colour characteristic of the aromatic monohydroxy-acids (*Ber.*, 1879, **12**, 1452), and a trace of the substance, when heated with soda-lime, gave a distinct phenolic odour.

A consideration of the composition and characters of the above-described substance indicated it to be *p*-hydroxyphenylacetic acid, which has not previously been observed to occur as such in the vegetable kingdom. It was obtained by A. G. Perkin and Newbury (Trans., 1899, **75**, 834) by the action of potassium hydroxide on genistein, and Ewins and Laidlaw (*J. Physiol.*, 1910, **41**, 78) have shown that when *p*-hydroxyphenylethylamine is administered by the mouth to an animal, it is transformed to a large extent into *p*-hydroxyphenylacetic acid, which may subsequently be extracted from the urine.

In order completely to establish the identity of the substance above described with *p*-hydroxyphenylacetic acid, it was deemed desirable to compare it with the synthetic acid, especially as it had been stated by Salkowski (*Ber.*, 1879, **12**, 1438), who first effected its synthesis, that its aqueous solution gives with ferric chloride a slight greyish-violet coloration, which immediately changes to a dirty greyish-green. It was, moreover, thought possible that the coloration given by the synthetic product might be due to a slight contamination with the corresponding ortho-compound, which is known to produce a violet colour with ferric chloride. Baumann (*Ber.*, 1880, **13**, 279), who obtained *p*-hydroxyphenylacetic acid from human urine, has, however, also noted that its aqueous solution gives with ferric chloride a slight violet coloration.

A quantity of the synthetic acid was accordingly prepared from phenylacetic acid, the latter having first been nitrated according to the method of Maxwell (*Ber.*, 1879, **12**, 1765). After very prolonged fractional crystallisation from warm water, a product was obtained which melted at 152°, the pure *p*-nitrophenylacetic acid having been observed by Maxwell (*loc. cit.*) to melt at 150°, and by Bedson (Trans., 1880, **37**, 91) at 150—151°. This nitro-acid was reduced by tin and hydrochloric acid, and then, by means of the diazo-compound, converted into the corresponding hydroxy-acid. The acid thus prepared was found to have the same melting point as that obtained from taraxacum root, and when the two products were mixed no depression of the melting point ensued. The reaction with Millon's reagent was precisely the same as that previously mentioned. On comparing the behaviour of the natural and the synthetic acid towards ferric chloride, it was observed in both cases that if a fairly concentrated solution of the acid were employed a faint and exceedingly fugitive violet coloration was produced, rapidly changing to greenish-brown, thus confirming the observations of Salkowski and of Baumann (*loc. cit.*).

The above results thus completely established the identity of the acid from taraxacum root with *p*-hydroxyphenylacetic acid.

After the extraction of the original aqueous liquid with ether, as above described, it was shaken with eighteen successive portions of warm amyl alcohol. These amyl-alcoholic liquids were united, washed with water, concentrated under diminished pressure to the consistency of a syrup, and the last traces of amyl alcohol removed by passing steam through the liquid. The syrupy product was then further concentrated under diminished pressure, afterwards on a water-bath, and finally dried as completely as possible in a vacuum desiccator. There was thus obtained a quantity (42·5 grams) of a dark brown, viscous mass, which possessed a strongly bitter taste, and in aqueous solution gave a dark green colour with ferric chloride.

Twelve grams of the above-mentioned product were heated for two hours with 5 per cent. sulphuric acid in aqueous alcohol. On subsequently distilling the mixture in a current of steam, a very small amount of a yellow oil was obtained, which gave the colour reaction of furfuraldehyde. The aqueous acid liquid was then extracted many times with ether, after which the sulphuric acid was removed by barium hydroxide, the excess of the latter by carbon dioxide, and the filtered liquid concentrated. From this syrupy product a small amount of an osazone (m. p. 210—211°) was prepared, thus indicating that some glucosidic material was contained in the amyl-alcoholic extract. The above-mentioned ethereal extract of the aqueous acid liquid was thoroughly extracted with aqueous ammonium carbonate, after which the ethereal liquid was dried and evaporated, but only a trace of yellow, amorphous material remained. On acidifying the ammonium carbonate extract, however, extracting many times with ether, and evaporating the solvent, a small amount of a crystalline substance was deposited. After recrystallisation from ethyl acetate this was obtained in thin, flat needles, melting at 146°, and was identical with the *p*-hydroxyphenylacetic acid, $C_8H_8O_3$, previously described. (Found, C=62·5; H=5·4. Calc., C=63·1; H=5·3 per cent.) The amount thus obtained was only 0·09 gram.

Another portion (27 grams) of the above-mentioned amyl-alcoholic extract was heated for a few minutes with a 10 per cent. solution of potassium hydroxide; the mixture then rapidly cooled and acidified, when a quantity of resinous material separated. This was collected, mixed with purified sawdust, and the dried mixture thoroughly extracted with ether. The aqueous acid liquid from which the resin had been removed was likewise extracted many times with ether, after which the two ethereal liquids were united and extracted with aqueous ammonium carbonate. On subsequently evaporating the ether there remained a slight residue, from which a crystalline substance melting at 233—235° was obtained. This substance was very soluble in chloroform, almost insoluble in ethyl acetate, and gave no coloration with ferric chloride, but the amount obtained (0·04 gram) was too small to permit of its further examination. The ammonium carbonate extract, when acidified and extracted with ether, yielded a small amount of a semi-crystalline product, which was readily soluble in warm water, and its solution gave with ferric chloride a deep green colour. The whole of this product was heated with chloroform containing a trace of ethyl acetate, when a small amount of a brown substance remained undissolved. The latter was crystallised from very dilute alcohol, when 0·07 gram of an acid was obtained, which melted and decomposed at 214°, and gave a deep green colour with ferric chloride. This substance was evidently 3:4-dihydroxycinnamic acid, since no depression of the melting point ensued when mixed with a pure specimen of the respective acid, and it was subsequently obtained in an amount which permitted of its complete identification, as will be further noted. The portion of the above-mentioned product which had dissolved in the mixture of chloroform and ethyl acetate formed, after the evaporation of the solvent, a viscid mass, which was repeatedly extracted with boiling benzene. From the latter liquid some crystals were deposited, which, after several crystallisations from benzene containing a little alcohol, separated in flat needles melting at 145—146°. This substance amounted to 0·25 gram, and was identified as *p*-hydroxyphenylacetic acid. (Found, C=62·6; H=5·4. Calc., C=63·1; H=5·3 per cent.)

After the extraction of the original aqueous liquid with amyl alcohol, as above described, the last traces of the latter were removed by a current of steam. The liquid was then treated with a solution of basic lead acetate until no further precipitate was produced, the precipitate collected and thoroughly washed with water, the washings being added to the main portion of the filtered liquid.

Isolation of 3:4-Dihydroxycinnamic Acid, $C_6H_3(OH)_2 \cdot CH:CH \cdot CO_2H$.

A portion of the above-mentioned basic lead acetate precipitate, representing 2 kilograms of the original alcoholic extract, was suspended in water, decomposed by hydrogen sulphide, and the mixture filtered. The filtered liquid was then concentrated under diminished pressure to the consistency of a thin syrup. It gave a dark brown coloration with ferric chloride, but no precipitate with gelatin, thus indicating the absence of tannin, and it also gave no reaction with potassium-mercuric iodide. As nothing separated from the liquid on keeping, it was heated to boiling, neutralised with potassium hydroxide, and sufficient of a concentrated solution of the latter added to represent about 10 per cent. of the mixture, after which it was boiled for about five minutes. The liquid was then poured into dilute sulphuric acid, and, after cooling, the mixture was extracted many times with ether, the combined ethereal liquids being subsequently extracted with aqueous ammonium carbonate and sodium hydroxide. Nothing of interest was removed by the last-mentioned alkali, and on finally evaporating the ether only a trace of amorphous material remained. The ammonium carbonate extract, however, after acidification and extraction with ether, yielded a product which gave with ferric chloride a dark green colour. From this product, after several crystallisations from hot water containing a little alcohol, a small amount (about 0·2 gram) of an acid was obtained, which melted and decomposed at 214—216° with evolution of gas. It was dried at 110°, and analysed:

0·0643 gave 0·1405 CO_2 and 0·0265 H_2O. C=59·6; H=4·6.

$C_9H_8O_4$ requires C=60·0; H=4·4 per cent.

The above-described substance was thus definitely identified as 3:4-dihydroxycinnamic acid, a smaller amount of which had previously been obtained from the amyl-alcoholic extract of the original aqueous liquid.

The filtrate from the precipitate produced by basic lead acetate was treated with hydrogen sulphide for the removal of the excess of lead, again filtered, and concentrated under diminished pressure to the consistency of a syrup. It evidently contained an abundance of sugar, since it readily yielded *d*-phenylglucosazone, melting at 204—206°. A portion of the syrup was acetylated, but as nothing crystalline separated from the product, even after long keeping, it was finally hydrolysed. The regenerated sugar was then found to be strongly lævorotatory, thus indicating that it must have consisted, to a large extent at least, of lævulose. Another portion of the syrup was heated for about two hours with 5 per cent. sulphuric acid, but, with the exception of traces of furfuraldehyde, it yielded nothing definite by this treatment. A further portion of the syrup was mixed with purified sawdust, and the dried mixture extracted successively in a Soxhlet apparatus with ether, chloroform, and ethyl acetate, but only small amounts of sugary material were thus removed.

The original syrupy liquid, when heated with an alkali hydroxide, developed a strongly basic, ammoniacal odour, and it gave an appreciable precipitate with a solution of iodine in potassium iodide.

Isolation of Choline, $C_5H_{15}O_2N$.

The main portion of the above-mentioned syrupy aqueous liquid was thoroughly extracted with alcohol, the resulting liquid evaporated, and the residue from the latter repeatedly treated with alcohol, in the same manner, until a product was finally obtained which was soluble in nearly absolute alcohol. By this means a large proportion of the sugar was eliminated, together with any other material which was sparingly soluble in alcohol. To the alcoholic solution thus obtained a saturated alcoholic solution of mercuric chloride was added, and the mixture kept in a closed vessel for a week. The precipitate which had then formed was collected, washed with a little alcohol, dissolved as completely as possible in warm water, and the solution filtered. The mercury was subsequently removed from this solution by hydrogen sulphide, the liquid again filtered, neutralised with sodium carbonate, then slightly acidified with hydrochloric acid, and finally evaporated to dryness, for the most part in a vacuum desiccator. The dry residue was treated with absolute alcohol, the filtered liquid evaporated, and the residue repeatedly so treated until free from inorganic salt.

A relatively small amount of a nearly colourless product was thus obtained, which deliquesced on exposure to the air, and the aqueous solution of which was precipitated by the usual alkaloidal reagents, as also by gold chloride. It possessed, in fact, all the recognised properties of choline chloride. A small portion of the substance was dissolved in a little water, and precipitated by a solution of auric chloride, the pale yellow precipitate being collected, washed with a little water, and dried at 100—105°:

0·0332 gave on ignition 0·0147 Au. Au = 44·3.
$C_5H_{14}ONCl,AuCl_3$ requires Au = 44·5 per cent.

Another portion of the substance was dissolved in absolute alcohol, and a solution of platinic chloride added. The resulting precipitate was collected, washed with a little alcohol, and dissolved in a small amount of water. After keeping for some time, reddish-brown plates were deposited, which melted and decomposed at 250—254°:

0·0460, when heated at 110°, lost 0·0010 H_2O. $H_2O = 2·2$.
0·0450 * gave on ignition 0·0143 Pt. Pt = 31·8.
0·0844 * ,, ,, 0·0269 Pt. Pt = 31·9.
$(C_5H_{14}ONCl)_2PtCl_4,H_2O$ requires $H_2O = 2·8$ per cent.
$(C_5H_{14}ONCl)_2PtCl_4$ requires Pt = 31·7 per cent.

The occurrence of choline as a constituent of taraxacum root has thus been established.

Examination of the Resin (B).

The crude resinous material which had been separated from the aqueous liquid (*A*), as previously described, was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a large Soxhlet apparatus with various solvents. The weights of the products, as determined by drying small, aliquot portions in a water-oven, were as follows:

Petroleum (b. p. 35—50°)	extracted	329·6	grams.
Ether	,,	19·6	,,
Chloroform	,,	10·0	,,
Ethyl acetate	,,	10·5	,,
Alcohol	,,	40·0	,,
	Total.........	409·7	grams.

As the above amount of resin was obtained from 7·3 kilograms of the original alcoholic extract, it is equivalent to about 1·8 per cent. of resin in the air-dried root.

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* Anhydrous substance.

Petroleum Extract of the Resin.

Identification of the Free Fatty Acids.

After the removal of the solvent from the petroleum extract the residue was dissolved in ether, and the ethereal liquid shaken successively with aqueous ammonium carbonate, sodium carbonate, and sodium hydroxide. The clear, alkaline liquids yielded, on acidification, only traces of fatty material, but both the sodium carbonate and sodium hydroxide produced, to some extent, emulsions, which were separated, and the ether removed, when a solid product was obtained. This consisted of the sodium salt of fatty acids. It was suspended in dilute sulphuric acid and warmed with chloroform, which removed about 15 grams of fatty acids. The latter were converted into their methyl esters, which were distilled three times under diminished pressure, and three fractions collected. The first two fractions consisted of methyl palmitate, melting at 27—28°. (Found, $C=75{\cdot}0$; $H=12{\cdot}7$. Calc., $C=75{\cdot}5$; $H=12{\cdot}6$ per cent.) The third fraction, which distilled at 206—208°/15 mm., was liquid and unsaturated:

0·2933 absorbed 0·3164 iodine. Iodine value=107·9.

For the further examination of this fraction it was converted into a lead salt, and the latter treated with ether. The portion insoluble in ether, when decomposed by hydrochloric acid, yielded 1·5 grams of a solid acid, which distilled between 230° and 235°/27 mm., and, after crystallisation, melted at 60—61°. It was identified as palmitic acid. (Found, $C=75{\cdot}0$; $H=12{\cdot}8$. Calc., $C=75{\cdot}0$; $H=12{\cdot}5$ per cent.) The portion of lead salt which was soluble in ether, when decomposed by hydrochloric acid, yielded 7 grams of liquid acids, which distilled between 220° and 235°/12 mm.:

0·1134 gave 0·3200 CO_2 and 0·1188 H_2O. $C=76{\cdot}9$; $H=11{\cdot}6$.
0·3898 absorbed 0·6111 iodine. Iodine value=156·8.

These results indicate that the liquid acids consisted essentially of a mixture of oleic and linolic acids, the latter predominating.

The ethereal liquid which had been shaken with aqueous alkalis, as above described, was subsequently evaporated, and the residue heated with an alcoholic solution of potassium hydroxide. The alcohol was then evaporated, water added, and the alkaline mixture extracted with ether, when a quantity of unsaponifiable material was removed, which will subsequently be described.

Identification of the Combined Fatty Acids.

Isolation of Melissic Acid, $C_{30}H_{60}O_2$.

During the above-mentioned extraction of the alkaline liquid with ether, a slight emulsion was formed. This was thoroughly washed with ether, then freed from the latter, and brought on a filter. A small amount of substance was thus collected, which proved to be the potassium salt of a fatty acid. The acid was liberated, dissolved in chloroform, and crystallised from ethyl acetate, when it melted at 87·5—88·5°, and amounted to 0·1 gram:

0·0821 gave 0·2399 CO_2 and 0·0983 H_2O. C=79·7; H=13·3.
$C_{30}H_{60}O_2$ requires C=79·7; H=13·3 per cent.

The small remaining portion of the acid was converted into its methyl ester, which, after crystallisation from alcohol, melted at 72—73°.

The above-described acid was thus identified as melissic acid, which, so far as is known to us, has never previously been obtained directly from a plant.

The aqueous alkaline liquid from which the unsaponifiable material had been removed by extraction with ether, as above described, was acidified and again extracted with ether. This ethereal liquid was dried, the solvent removed, and the residual fatty acids converted into their methyl esters. The latter, when distilled under diminished pressure, passed over between 180° and 270°/9 mm., and amounted to about 55 grams. They were optically inactive. The esters were then hydrolysed, and the resulting product, which consisted of a mixture of saturated and unsaturated acids, was separated into liquid and solid portions by means of the lead salts.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over between 215° and 265°/18 mm., and amounted to about 40 grams. An analysis and a determination of the iodine value gave the following results:

0·1343 gave 0·3800 CO_2 and 0·1393 H_2O. C=77·2; H=11·5.
0·3100 absorbed 0·4448 iodine. Iodine value=143·5.
$C_{18}H_{34}O_2$ requires C=76·6; H=12·1 per cent. Iodine value=90·1.
$C_{18}H_{32}O_2$,, C=77·1; H=11·4 ,, ,, ,, ,, =181·4.
$C_{18}H_{30}O_2$,, C=77·7; H=10·8 ,, ,, ,, ,, =274·1.

The above results would indicate that the liquid acids consisted chiefly of a mixture of oleic and linolic acids, with possibly a little linolenic acid.

The Solid Acids.—These acids, which amounted to 10 grams, were fractionally crystallised from ethyl acetate. The least soluble fraction so obtained separated in small needles, which melted quite constantly at 82—84°:

0·0673 gave 0·1946 CO_2 and 0·0820 H_2O. C=78·8; H=13·5.
$C_{27}H_{54}O_2$ requires C=79·0; H=13·2 per cent.

This acid was thus identified as cerotic acid, although the melting point was somewhat higher than that usually assigned to it.

The next two fractions, of lower melting point (75—77°), also appeared to consist essentially of cerotic acid, since they gave on analysis the following figures: C=78·5; H=13·2 per cent.

The most readily soluble fractions, which melted at 56—58°, were distilled under diminished pressure, when practically the whole passed over between 205° and 207°/12 mm. After one crystallisation of the product it melted at 60—61°, and was identified as palmitic acid. (Found, C=75·0; H=12·7. Calc., C=75·0; H=12·5 per cent.)

Unsaponifiable Constituents of the Petroleum Extract.

The ethereal liquid, obtained by extracting the hydrolysed petroleum extract of the resin with ether, as above described, was dried, and the solvent removed, when 125 grams of a yellow solid were obtained. An attempt was first made to separate the constituents of this material by direct fractional crystallisation, but, as this was unsuccessful, the various fractions were separately acetylated, and the resulting products subjected to prolonged fractional crystallisation. The solvents employed for this purpose were ethyl acetate and a mixture of the latter with alcohol.

Isolation of a New Monohydric Alcohol, Taraxasterol, $C_{29}H_{47}\cdot OH$.

After many crystallisations of the above-mentioned acetylated products, a small fraction (5·2 grams) was obtained, which separated in handsome, colourless, hexagonal plates, melting at 251—252°, and this melting point was not changed by further crystallisation. A portion of this acetyl derivative was hydrolysed by boiling it for three or four hours with an alcoholic solution of potassium hydroxide, after which the alcohol was for the most part removed, water added, and the resulting solid collected. On crystallisation from alcohol, it separated in long, colourless needles, melting at 221—222°:

0·1999, when heated at 125°, lost 0·0198 H_2O. H_2O=9·9.
0·0848 * gave 0·2625 CO_2 and 0·0902 H_2O. C=84·4; H=11·8.
0·0737 * „ 0·2284 CO_2 „ 0·0772 H_2O. C=84·5; H=11·6.
$C_{29}H_{48}O,2\frac{1}{2}H_2O$ requires H_2O=9·8 per cent.
$C_{29}H_{48}O$ requires C=84·5; H=11·6 „ „

It is evident from these results that the above-described compound possesses the formula $C_{29}H_{48}O$, and, being a new alcohol, having properties similar to those of the phytosterols, it is proposed to

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* Dried at 120°.

designate it *taraxasterol*, with reference to the source from which it has been obtained.

A determination of its optical rotatory power gave the following result:

0·4343,* made up to 20 c.c. with chloroform, gave α_D +4°11′ in a 2-dcm. tube, whence $[\alpha]_D$ +96·3°.

Taraxasterol is homologous with two monohydric alcohols previously isolated in these laboratories from the rhizome of *Apocynum androsæmifolium*, namely, androsterol, $C_{30}H_{50}O$, and homo-androsterol, $C_{27}H_{44}O$ (Trans., 1909, **95**, 739), and it gives a colour reaction similar to that yielded by the last-mentioned compounds; thus, if a small amount of the substance be dissolved in chloroform with a little acetic anhydride, and a few drops of concentrated sulphuric acid subsequently added, a pink colour is produced, which slowly changes to a dark magenta with a green fluorescence, and this colour persists for several hours. The above-mentioned alcohols, together with a homologue of taraxasterol to be subsequently described, $C_{25}H_{40}O$, constitute four members of a group which is represented by the general formula $C_nH_{2n-10}O$.

Acetyltaraxasterol, $C_{29}H_{47}O\cdot CO\cdot CH_3$.—This compound (m. p. 251—252°), the preparation and characters of which have already been described, was dried at 120° and analysed:

0·0866 gave 0·2602 CO_2 and 0·0854 H_2O. C=81·9; H=10·9.
0·0824 „ 0·2472 CO_2 „ 0·0810 H_2O. C=81·8; H=10·9.
$C_{31}H_{50}O_2$ requires C=81·9; H=11·0 per cent.

A determination of its optical rotatory power gave the following result:

0·2046,* made up to 20 c.c. with chloroform, gave α_D +2°30′ in a 2-dcm. tube, whence $[\alpha]_D$ +122·2°.

Monobromoacetyltaraxasterol, $C_{29}H_{46}BrO\cdot CO\cdot CH_3$.—Half a gram of the above-described acetyl derivative was dissolved in chloroform, and to the cold solution a slight excess of a solution of bromine in the same solvent was slowly added. The product was crystallised from ethyl acetate, when it separated in small, colourless needles, melting at 233—234°:

0·1204 gave 0·0421 AgBr. Br=14·9.
$C_{31}H_{49}O_2Br$ requires Br=15·0 per cent.

Benzoyltaraxasterol, $C_{29}H_{47}O\cdot CO\cdot C_6H_5$.—This derivative was prepared by heating the respective alcohol for a short time with benzoyl chloride and a few drops of pyridine. The product, after several crystallisations from a mixture of alcohol and chloroform, separated in glistening leaflets melting at 232°:

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* Dried at 120°.

0·0810 * gave 0·2471 CO_2 and 0·0728 H_2O. C=83·2; H=10·0.
$C_{36}H_{52}O_2$ requires C=83·7; H=10·1 per cent.

Other well-crystallised fractions obtained from the original acetylated product above described possessed the following characters:

I. M. p. 216—222°; $[\alpha]_D$ +68·1°; C=81·7; H=10·9 per cent.
II. M. p. 225—227°; $[\alpha]_D$ +62·2°; C=81·5; H=11·1 „ „
III. M. p. 225—235°; $[\alpha]_D$ +77·8°; C=81·6; H=11·3 „ „

The composition and characters of these fractions indicated them to contain a substance analogous to taraxasterol, but having a lower melting point and a lower optical rotation. The mother-liquors from these fractions were evaporated, and the residues brominated. By the fractional crystallisation of the product, a further amount of the above-described monobromoacetyltaraxasterol was obtained.

Fractions of the acetylated product melting lower than those above mentioned could only be crystallised with difficulty. The mother liquors from these fractions were evaporated to dryness, the residues hydrolysed, and then treated with phthalic anhydride, both in the dry state and with the admixture of a little pyridine or xylene. No acid phthalic ester could, however, be isolated by this treatment.

Isolation of a New Monohydric Alcohol, Homotaraxasterol, $C_{25}H_{39}\cdot OH$.

The above-mentioned difficultly crystallisable fractions of acetylated material were united, hydrolysed, and the product distilled under diminished pressure, when practically the whole passed over between 335° and 340°/25 mm. The distillate, which was contaminated with some oily material, was purified by dissolving it in petroleum of high boiling point, and treatment with animal charcoal. A product was thus obtained, which, after several crystallisations from dilute alcohol, separated in small needles melting constantly at 163—164°. The substance did not undergo any appreciable loss in weight on drying at 120°, and the total amount obtained was 0·45 gram:

0·0741 gave 0·2280 CO_2 and 0·0770 H_2O. C=83·9; H=11·5.
$C_{25}H_{40}O$ requires C=84·3; H=11·2 per cent.

The composition of this substance clearly indicated it to be a lower homologue of the above-described taraxasterol, and it yielded precisely the same colour reaction as the latter. Being also a new compound it is proposed to designate it *homotaraxasterol.*

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* Dried at 120°.

A determination of its optical rotatory power gave the following result:

0·0989, made up to 20 c.c. with chloroform, gave α_D +0°15′ in a 2-dcm. tube, whence $[\alpha]_D$ +25·3°.

Acetylhomotaraxasterol, $C_{25}H_{39}O\cdot CO\cdot CH_3$.—This compound was prepared by heating the respective alcohol with acetic anhydride. It separated from a mixture of ethyl acetate and alcohol in small, colourless needles, melting at 219—220°:

0·0654 gave 0·1943 CO_2 and 0·0645 H_2O. C=81·0; H=10·9.
$C_{27}H_{42}O_2$ requires C=81·4; H=10·5 per cent.

0·0888, made up to 20 c.c. with chloroform, gave α_D +0°15′ in a 2-dcm. tube, whence $[\alpha]_D$ +28·1°.

A very small portion of homotaraxasterol was converted into its *benzoyl* derivative, which separated from a mixture of chloroform and alcohol in small, flat needles, melting at 202°. The amount of this compound was not sufficient for analysis.

Ether Extract of the Resin.

This extract was considerably concentrated in volume and kept for some time, when a small amount of a sparingly soluble grey substance was deposited. This was collected, and the clear, ethereal liquid then extracted successively with aqueous ammonium carbonate and sodium carbonate, which, however, removed only traces of brown, amorphous material. The ethereal liquid was finally extracted with aqueous potassium hydroxide, and the alkaline liquid acidified and extracted with ether, which removed some amorphous material, and at the same time an emulsion was formed. This was separated, washed with a little ether, and the latter removed by a current of air, when, on filtration, a further small amount of the above-mentioned grey substance was obtained. The ethereal liquid which had been extracted with alkalis, when dried and evaporated, also yielded a little of the same sparingly soluble grey substance.

Isolation of Cluytianol, $C_{29}H_{46}O(OH)_4$.

The above-described grey substance was first subjected to prolonged extraction with absolute alcohol in a Soxhlet apparatus. During this operation it was partly deposited in a nearly white condition, and, on finally concentrating the alcoholic liquid, practically all the substance separated. The material thus obtained amounted to 4·1 grams. It was subsequently heated with acetic anhydride, and the resulting product fractionally crystallised many times from alcohol, when an acetyl derivative was obtained, which separated in colourless, flat needles, melting at 161°.

A portion of the acetyl derivative was hydrolysed by boiling with an alcoholic solution of potassium hydroxide. The product, after crystallisation from dilute pyridine, separated in minute, colourless crystals, melting and decomposing at 297°:

0·0826 gave 0·2197 CO_2 and 0·0790 H_2O. C = 72·5; H = 10·6.

$C_{29}H_{50}O_5$ requires C = 72·8; H = 10·5 per cent.

Although this substance agrees in its empirical composition with ipuranol, $C_{29}H_{47}O_2(OH)_3$, a trihydric alcohol which has been obtained in these laboratories from many sources, and also yields the same colour reaction as ipuranol, the analysis and characters of its derivatives proved it to be identical with a new tetrahydric alcohol, $C_{29}H_{46}O(OH)_4$, recently isolated by Tutin and Clewer from the South African plant *Cluytia similis*, Muell. Arg., and designated by them cluytianol (this vol., p. 2230).

Tetra-acetylcluytianol, $C_{29}H_{46}O_5(CO{\cdot}CH_3)_4$.—This compound (m. p. 161°) was prepared as above described:

0·0820 gave 0·2064 CO_2 and 0·0673 H_2O. C = 68·6; H = 9·1.

Its molecular weight was determined by Mr. H. W. B. Clewer:

0·4326, in 26·45 of benzene, gave $\Delta t - 0{\cdot}12°$. M.W. = 668.

$C_{37}H_{58}O_9$ requires C = 68·7; H = 9·0 per cent. M.W. = 646.

A determination of its optical rotatory power gave the following result:

0·1976, made up to 20 c.c. with ethyl acetate, gave $\alpha_D - 0°24'$ in a 2-dcm. tube, whence $[\alpha]_D - 20{\cdot}2°$.

Tetrabenzoylcluytianol, $C_{29}H_{46}O_5(CO{\cdot}C_6H_5)_4$.—A little of this compound was prepared by treating the respective alcohol with benzoyl chloride in the presence of pyridine. The product, after repeated crystallisation from a mixture of chloroform and alcohol, separated in small, colourless needles, melting at 196°:

0·0620 gave 0·1733 CO_2 and 0·0443 H_2O. C = 76·2; H = 7·9.

$C_{57}H_{66}O_9$ requires C = 76·5; H = 7·4 per cent.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

These extracts were dark brown, amorphous products, and amounted to 10, 10·5, and 40 grams respectively. They were separately examined, but nothing definite could be isolated from them. The ethyl acetate and alcohol extracts were therefore heated with dilute sulphuric acid in aqueous alcohol, and the mixture distilled in a current of steam. The distillate contained traces of an oily substance, which gave the colour reaction of furfuraldehyde, but no sugar appeared to be produced, and the extracts were evidently not glucosidic.

Summary and Conclusions.

The material employed for this investigation consisted of the air-dried, fresh roots of taraxacum (*Taraxacum officinale*, Wiggers), collected in the autumn from plants grown in England.

The roots were found to contain a very small amount of an enzyme, which slowly hydrolysed amygdalin.

An alcoholic extract of the root, when distilled in a current of steam, yielded a small amount of a yellow essential oil. From the portion of the extract which was soluble in water, the following substances were isolated: (i) *p*-hydroxyphenylacetic acid, $C_8H_8O_3$ (m. p. 144—146°); (ii) 3:4-dihydroxycinnamic acid, $C_9H_8O_4$ (m. p. 214—216°); (iii) a small amount of choline, $C_5H_{15}O_2N$, which was identified by its gold and platinum compounds. The aqueous liquid contained, furthermore, a considerable quantity of a lævorotatory sugar, which appeared to consist chiefly, if not entirely, of lævulose, and yielded an osazone, melting at 204—206°.

The portion of the alcoholic extract which was insoluble in water consisted of a soft, oily resin, which amounted to 1·8 per cent. of the weight of the root. From this material the following compounds were isolated: (i) a new monohydric alcohol, *taraxasterol*, $C_{29}H_{47}\cdot OH$ (m. p. 221—222°; $[\alpha]_D$ $+96\cdot3°$), which yielded an *acetyl* derivative (m. p. 251—252°; $[\alpha]_D$ $+122\cdot2°$), a *monobromoacetyl* derivative (m. p. 233—234°), and a *benzoyl* derivative (m. p. 232°); (ii) a new monohydric alcohol, *homotaraxasterol*, $C_{25}H_{39}\cdot OH$ (m. p. 163—164°; $[\alpha]_D$ $+25\cdot3°$), which yielded an *acetyl* derivative (m. p. 219—220°; $[\alpha]_D$ $+28\cdot1°$), and a *benzoyl* derivative (m. p. 202°). The above-mentioned alcohols, together with two previously isolated compounds, androsterol, $C_{30}H_{49}\cdot OH$, and homoandrosterol, $C_{27}H_{43}\cdot OH$ (Trans., 1909, **95**, 739), constitute an homologous group, which is represented by the general formula $C_nH_{2n-10}O$. (iii) Cluytianol, $C_{29}H_{46}O(OH)_4$, melting at 297° (this vol., p. 2230), from which the tetra-acetyl and tetrabenzoyl derivatives were prepared; (iv) palmitic, cerotic, and melissic acids, together with a mixture of unsaturated acids, consisting chiefly of oleic and linolic acids, with, apparently, a little linolenic acid.

The bitter taste of taraxacum, which has hitherto been ascribed to the so-called "taraxacin," appears to be due chiefly to dark-coloured, amorphous material, and not to any distinct principle. It was found, for example, that the portion of an alcoholic extract of the root which is soluble in water, when repeatedly extracted with warm amyl alcohol, yielded a viscous product, which possessed an intensely bitter taste.

A consideration of the results of the present investigation renders it evident that the products which many years ago received the designations of "taraxacin" and "taraxacerin" were not only indefinite in character, but must have consisted of very complex mixtures. It is therefore desirable that these names should no longer be retained in the literature.

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CCLIII.—*The Purification, Density, and Expansion of Ethyl Acetate.**

By JOHN WADE, D.Sc., and RICHARD WILLIAM MERRIMAN, M.A.

THE results of the determinations at different temperatures of the density of ethyl acetate published by many different workers vary so much from each other that the authors thought it worth while to redetermine these constants with carefully purified material.

One factor which helped to make previous determinations inaccurate was the faulty methods used for the estimation of the densities.

Most pyknometers possess the following defects: (*a*) the ground-in stoppers or caps are not absolutely efficient in preventing loss or entry of air, due to the expansion or contraction of the liquid, after removal from the thermostat; (*b*) the dissolved air is not removed during filling; (*c*) moist air can get in contact with the liquid during filling, and whilst in the thermostat.

The present authors decided to return once more to the use of Gay-Lussac's pyknometer, which was amenable to improvements that would eliminate all the above-mentioned defects. The instrument is sketched in Fig. 1, which represents one holding 25 c.c. of liquid. The capillary of the stem, on which is scratched the circular mark M, is 0·7 mm. in diameter, so that an error of 0·01 mm. in the adjustment of the height of the liquid would represent an error in weight of about 0·003 milligram or in temperature of 0·0001°.

In order to fill the pyknometer with the liquid a special filling apparatus,† shown in the figure, was designed. The thick-walled

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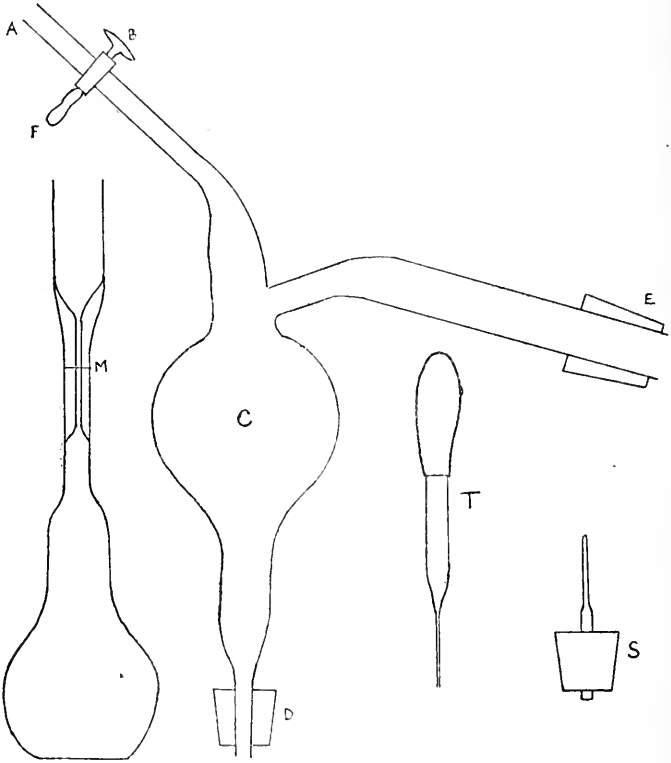
* The experimental work in this and the succeeding communication was completed at the time of Dr. Wade's death, and the results deduced from the work are here collected together.—R. W. M.

† Specimens of the apparatus described were made to the satisfaction of the authors by Messrs. A. Gallenkamp.

test-tube or the round-bottomed flask containing the liquid is fixed on the rubber stopper *E*. The neck of the pyknometer is joined to the rubber stopper *D*. The end *A* is connected with an air-pump, and the end *F* of the three-way tap *B* with a calcium chloride tower. The apparatus is exhausted; then, by tilting the instrument, the liquid is run into the bulb *C*; the tap *B* is now turned so as to admit dry air, which forces the liquid into the pyknometer. The process is repeated once or twice until the pyknometer is nearly

FIG. 1.



filled with the liquid. Then the pump is kept working until all the dissolved air has left the liquid, the pyknometer being tapped to disengage the air bubbles. Dry air is admitted once more, and the instrument completely fills with the liquid, except perhaps for a minute air-bubble at the bottom of the capillary. On warming the liquid slightly by holding the pyknometer in the hand, the expansion drives out this bubble. An amount of liquid is left in the neck to allow for the contraction when the pyknometer is placed in the constant-temperature bath. The instrument is removed from *D*, the neck rapidly dried with filter paper, and tightly closed with a rubber stopper. The pyknometer is now placed in the thermostat, immersed right up to the mark. After two hours the level of the liquid is rapidly and approximately adjusted to the mark by means of the capped tube *T* drawn out to a very fine capillary. The stopper is replaced, and the thermometer and the level of the liquid are carefully observed. When both have been steady for fifteen minutes the liquid is adjusted accurately to the mark. The neck and capillary above the mark are now dried with filter paper, and air blown by means of bellows through the neck to remove completely the vapour of the liquid. A newly-weighed rubber stopper, which tightly fits the neck, is firmly pressed in to the same mark each time,* and the pyknometer is removed from the thermostat, cooled, or warmed by the hand or by water to the temperature of the balance case, dried, and finally polished with a piece of cambric. It is left in the balance case for fifteen minutes and weighed by substitution, with weights which have been calibrated in the same way. A distinct advantage of the method is that the weighing can be performed at leisure, as the air and vapour are absolutely imprisoned.

In the view of the authors, the density of a liquid, determined for critical purposes, should always be done at 0°, as the temperature is independent of any thermometer.

The water contents of the pyknometer at different temperatures are determined as previously described by the authors (Trans., 1909, **95**, 2180, footnote). The formula used for the calculation of the density is number VI in the same paper (*ibid.*, p. 2180), which gives results correct to 3 in the sixth place of decimals. If absolute accuracy is required, the full formula (*ibid.*, p. 2176, footnote) must be used, or the following formula:

$$Dt^\circ/t^\circ = \frac{W\{1+\sigma(\Omega/W\rho - 1/B)\}}{W_1\{1+\sigma_1(\Omega_1/W_1 d - 1/B)\}},$$

where W_1 = apparent weight of water; W = apparent weight of liquid; σ_1 = density of air when water was weighed; σ = density of air when liquid was weighed; d = density of water at t°; ρ = density of liquid found by formula VI; $\Omega_1 = W_1 + \Omega_1\sigma_1$; $\Omega = W + \Omega_1\sigma$; B = density of brass. The denominator of the fraction is determined once for all at each temperature.

All sorts of refinements, such as the use of a counterpoise or

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* In forcing in the stopper, it would require an error of as much as 1·5 mm. to affect the fifth place of decimals. The volume of the stopper up to the mark, used in applying the buoyancy correction, need only be known approximately (within 30 per cent.), as it also occurs in the water-content of the pyknometer.

precautions in weighing (Manley, *Phil. Trans.*, 1910, **210**, *A*, 387), can be used with this method, but the authors found that an accuracy of one in the fifth place could be attained with a 25 c.c. pyknometer, without the use of a counterpoise (Trans., 1909, **95**, 2178, footnote). With a balance weighing to 0·01 milligram and using a counterpoise, the method would give results accurate to one in the sixth place of decimals, but it must be borne in mind that in this case the actual temperature must be known with absolute accuracy to 0·001°.

A test of the method was undertaken by preparing a large sample of dry alcohol, and determining its density under all kinds of atmospheric conditions.

TABLE I.

Density of Alcohol under Different Atmospheric Conditions.

Temp.	Barometer.	Density at 0°/4°.
15°	760	0·80629
18	770	0·80630
12·5	753	0·80629
20	750	0·80629
11	775	0·80630

It might be thought that when pressing in the weighed rubber stopper some air could escape if the stopper were held unevenly when commencing to force it in. This point was tested in the following manner. A one-holed stopper * was used containing a short glass tube, open at the bottom and drawn out to an extremely fine point at the top (*S* in figure). This stopper was weighed and pressed in as before when doing both the water content and the density of the liquid. Before removing from the ice, the fine tip was sealed by momentarily touching it with a flame. The density of the above alcohol under these conditions was 0·80629 $\frac{0°}{4°}$.

The method of emptying the pyknometer is simple, and preserves the liquid in its original condition. A bubble of air is introduced into the pyknometer by means of the instrument *T*. The pyknometer is joined to *D* of the filler, which is filled with dry air. At *E* is placed a round-bottomed flask filled with dry air. The apparatus is tilted so that the pyknometer is inverted, and when the pump is started the liquid flows into the flask. The flask is removed, and *E* is closed with a rubber stopper. If the exhaustion and the introduction of dry air through *F* are repeated several times the pyknometer is thoroughly dried and ready for the next density determination.

The water content of the pyknometer changes in the same way

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* Of course, in this experiment, the stopper need not be forced in to any particular mark.

as the zero of a thermometer, and should be redetermined every three months.

Another adverse factor in earlier determinations of the density of ethyl acetate was the imperfect methods of preparing and purifying the ester. The continuous method described a few years ago (Wade, Trans., 1905, **87**, 1656) proved a very convenient one for the preparation of the large quantity of ethyl acetate used in this investigation.

I.—*Purification of Ethyl Acetate.*

(*a*) The product of the continuous method (*loc. cit.*) was distilled three times on the water-bath from a large quantity of water. The resulting ester was roughly dried with desiccated potassium carbonate. Water (2 grams) was added to 500 grams of this ester, and the whole distilled through a Young evaporator column. In this way the small quantity of alcohol still left in the ester, together with the excess of water, were removed in the first fractions in the form of azeotropic mixtures, whilst the later fractions and the residue in the flask consisted of pure dry ester. The temperatures are on the hydrogen scale reduced to 760 mm. in the latitude of Paris.

Fractionation (a). *Partly Pure Ester,* 500 *grams; Water,* 2 *grams.*

Fraction.	Temp.	Weight.	Δ %.	Fraction.	Temp.	Weight.	Δ %.
a	69·0 —72·00°	22·00	1·5	*f*	77·09—77·11°	35·60	35·5
b	72·00—73·00	23·85	4·8	*g*	77·11—77·13	41·50	414·0
c	73·00—73·20	25·60	25·5	*h*	77·13—77·14	45·00	898·0
d	73 20—77·01	60 00	3·1	*i*	77·14—77·15	50·00	**996·0**
e	77·01—77·09	43·40	10·8				

Residue = 154 grams.

The densities of fractions *h* and *i* were $0{\cdot}92454\,\frac{0^\circ}{4^\circ}$ and $0{\cdot}92457\,\frac{0^\circ}{4^\circ}$ respectively.

(*b*) The later fractions and residue of the above fractionation were mixed and distilled four times from large quantities of water, dried with desiccated potassium carbonate for two days, and with phosphoric oxide for twelve hours. The ester was poured off from the discoloured phosphoric oxide and fractionated through an eight-section Young evaporator column.

Fractionation (b). *Ester,* 300 *grams.*

Fraction.	Temp.	Weight.	Δ %.	Fraction.	Temp.	Weight.	Δ %.
a	76·73—77·04°	22·00	25	*e*	77·13—77·14°	45·50	1517
b	77·04—77·08	21·30	177	*f*	77·14—77·15	89·40	**2913**
c	77·08—77 11	22·50	250				
d	77·11—77·13	23·00	383				

Residue = 75·3 grams.

The densities of fractions *c* and *f* were $0{\cdot}92454\,\frac{0^\circ}{4^\circ}$ and $0{\cdot}92455\,\frac{0^\circ}{4^\circ}$ respectively.

(*c*) Another preparation was treated as in (*b*), and fractionated.

Fractionation (c). *Ester*, 200 *grams*.

Fraction.	Temp.	Weight.	Δ %.
a	77·05—77·13°	30·50	191
b	77·13—77·14	45·00	2250
c	77·14—77·15	74·50	3725

Residue = 49 grams.

The density of fraction (*c*) was 0·92455 $\frac{0^\circ}{4^\circ}$ and that of the residue 0·92453 $\frac{0^\circ}{4^\circ}$.

(*d*) Another preparation treated as in (*b*) and (*c*).

Fractionation (d). *Ester*, 200 *grams*.

Fraction.	Temp.	Weight.	Δ %.
a	77·06—77·12°	30·0	150
b	77·12—77·14	50·5	1262
c	77·14—77·15	99·5	4975

Residue = 19 grams.

The densities of fractions *b* and *c* were each 0·92453 $\frac{0^\circ}{4^\circ}$.

The following eight densities for pure ethyl acetate were thus obtained:

0·92454	Fractionated with a little water.
0·92457	
0·92454	Dried with phosphoric oxide, poured off, and fractionated.
0·92455	
0·92455	
0·92453	
0·92453	
0·92453	

Mean value **0·92454** 0$\frac{0^\circ}{4^\circ}$.

During the above fractionations the usual precautions were taken against the absorption of adventitious moisture.

Young and Thomas (Trans., 1893, **63**, 1216) distilled their specimens on the water-bath from the phosphoric oxide used in drying them, and obtained densities of 0·92438 $\frac{0^\circ}{4^\circ}$ and 0·92434 $\frac{0^\circ}{4^\circ}$.

The low densities might be due to a small amount of decomposition produced by heating the ester in contact with the phosphoric oxide, with the gradual accumulation of a small amount of alcohol. In order to test this, the following experiment was performed. A little phosphoric oxide was added to some pure ester, and the mixture fractionated through an evaporator column.

Fractionation (e). *Ester*, 200 *grams*; P_2O_5, 2 *grams*.

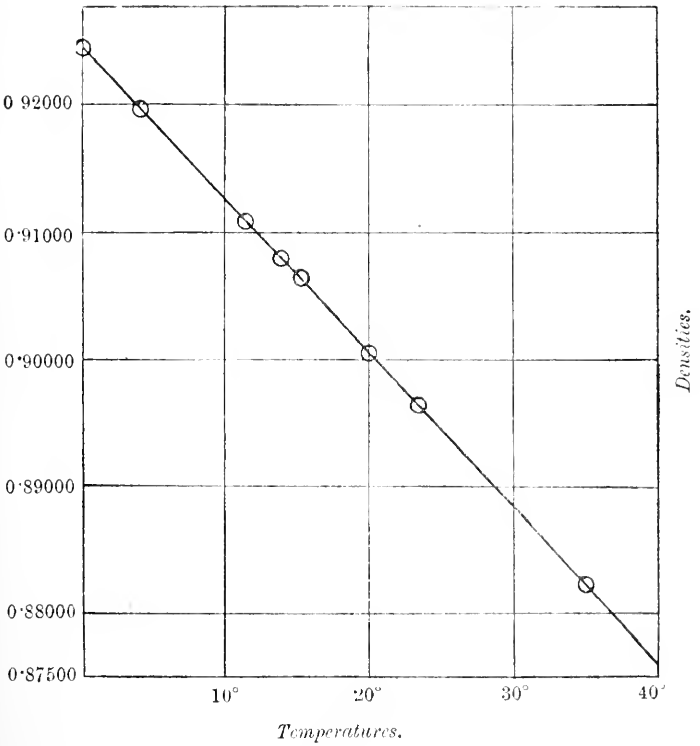
Fraction.	Temp.	Weight.	Δ %.
a	77·00—77·12°	24·70	106
b	77·12—77·13	100·00	4950
c	77·13—77·14	45·50	2253

Residue = 29 grams.

The densities of fractions *b* and *c* were 0·92448 $\frac{0^\circ}{4^\circ}$ and 0·92440 $\frac{0^\circ}{4^\circ}$. The residue was distilled off to dryness from the water-bath, and had a density of 0·92421 $\frac{0^\circ}{4^\circ}$.

The low densities of the distillates, and especially of the residue, showed that a small amount of decomposition had been brought about by distilling the ester with phosphoric oxide. Pure ethyl acetate should be prepared by fractionating the ester with a little water and rejecting the first third of the distillate, or by drying with phosphoric oxide in the cold, pouring off, and fractionating.

Fig. 2.



II.—*The Expansion of Ethyl Acetate.*

The densities at different temperatures were determined in the way described in the previous paper. The bath in which the pyknometer was immersed consisted of a large Dewar vacuum vessel, immersed in a large bath of water provided with a stirrer. The top of the Dewar vessel was tightly closed with a sheet of asbestos with holes for the neck of the pyknometer, thermometer, and a stirrer.

For temperatures below atmospheric the water in the vacuum vessel was a little warmer than that in the bath. The temperature of the water in the bath slowly rose, whilst that of the water in the vacuum vessel slowly fell. When the two temperatures became equal, that of the vacuum vessel remained constant sufficiently long for the adjustments of the liquid in the pyknometer to be completed. For temperatures above atmospheric the temperature of the outer bath was a little higher than that of the water in the vacuum vessel at the commencement of the experiment.

An Anschütz thermometer, which had been compared with standards, was used, and could be read to 0·01° by means of a lens. The temperatures recorded are reduced to the hydrogen scale.

Fig. 3.

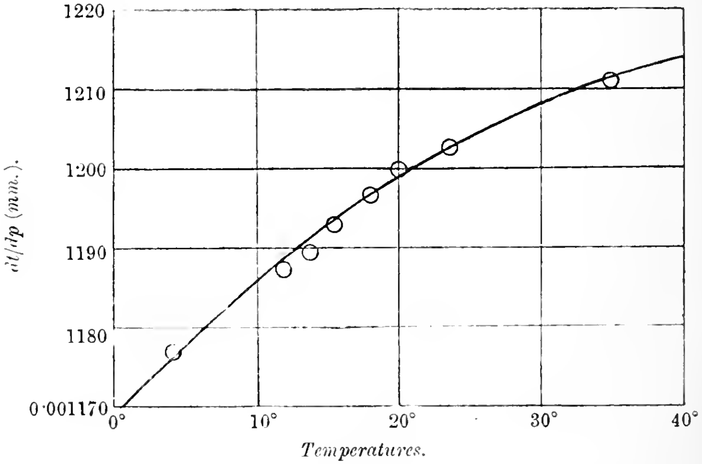


TABLE I.

Temp.	Density, $t^\circ/4^\circ$.	$\frac{d\,0^\circ/4^\circ - d\,t^\circ/4^\circ}{t}$
0·00°	0·92454	—
4·13	0·91968	0·001177
11·82	0·91051	0·001187
13·92	0·90799	0·001189
15·32	0·90625	0·001193
17·98	0·90301	0·001197
20·00	0·90053	0·001200
23·45	0·89634	0·001203
34·83	0·88236	0·001211

The densities plotted against temperature are shown in Fig. 2, and the values in the last column plotted against temperature are shown in Fig. 3. The values of $(d^{0^\circ}_{4^\circ} - d^{t^\circ}_{4^\circ})/t$ were smoothed by the aid of the curve, and the following values for the densities were obtained:

Temp.	Density, $t°/4°$.	$\frac{d\,0°/4° - d\,t°/4°}{t}$.
0°	0·92454	—
5	0·91865	0·0011775
10	0·91268	0·001186
15	0·90665	0·001193
20	0·90056	0·001199
25	0·89446	0·0012035
30	0·88830	0·001208
35	0·88214	0·0012115
40	0·87598	0·001214

To calculate the density at any temperature between 0° and 40° the following formula is used:

$$\Delta t = -0{\cdot}00000002t^3 + 0{\cdot}00000195t^2 + 0{\cdot}001168t.$$

Δt is then subtracted from 0·92454, and the result gives the density at $t°/4°$, within 5 in the sixth place of decimals.

TABLE III.

Comparison with Young and Thomas (Trans., 1893, **63**, 1216).

	Wade and Merriman.		Young and Thomas.	
Temp.	Density, $t°/4°$.	$\frac{d\,0°/4° - d\,t°/4°}{t}$.	Density, $t°/4°$.	$\frac{d\,0°/4° - d\,t°/4°}{t}$.
18·15°	0·90282	0·001197	0·90286	0·001187
19·90	0·90068	0·001199	0·90070	0·001190
0	0·92454	—	0·92436 (mean)	—

It will be noticed that the results of Young and Thomas at the higher temperatures are almost identical with those of the present authors, whilst at 0° their density is distinctly lower. This may be due to the difficulties in determining the density at 0° by the method used by them, or, as before suggested (p. 2434), due to the presence of a little alcohol, which will cause the expansion to be less than that of pure ethyl acetate.

TABLE IV.

Comparison with Perkin (Trans., 1884, **45**, 492).

Wade and Merriman.	Perkin.
0·90744 15°/15°	0·90724 15°/15°
0·90665 15°/4°	0·90645 15°/4°
0·89446 25°/4°	0·89449 25°/4°

Again, for the same reasons, the expansion obtained by Perkin is less than that found by the present authors.

TABLE V.

Specific Volumes.

Observer.	0°.	10°.	20°.	30°.
Elsässer (*Annalen*, 1883, **218**, 306) ...	1	1·01263	0·02613	1·04045
Wade and Merriman	1	1·01301	1·02663	0·04080
Zander (quoted by Elsässer, *loc. cit.*)	1	1·01353	1·02728	1·04142

The results of the present authors are nearly midway between those of Zander and Elsässer.

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CCLIV.—*The Vapour Pressure of Ethyl Acetate from 0° to 100°.*

By JOHN WADE, D.Sc., and RICHARD WILLIAM MERRIMAN, M.A.

HAVING prepared large quantities of pure ethyl acetate for the work described in the preceding communication, the authors thought it worth while to find its vapour pressure at various temperatures, especially as they had at their command means of maintaining constant pressures not hitherto at the disposal of other workers (Trans., 1911, **99**, 984).

I.—For temperatures above 15° the boiling point was determined at constant pressure in the manner described in the above-mentioned paper (*ibid.*, p. 989). At each pressure a complete fractionation of 100 grams of pure ethyl acetate was made, the temperature recorded being that at which Δ per cent. was a maximum (see Wade, Trans., 1905, **87**, 1656).

TABLE I.

Experimental Boiling Points of Ethyl Acetate.

Pressure in mm.	Boiling point.	*dt/dp.*	Pressure. in mm.	Boiling point.	*dt/dp.*
60	16·20°	0·325	612	70·78°	0·048
73	20·00	0·28	760	77·15	0·04
78	21·30	0·27	900	82·40	0·035
175	38·48	0·14	980	85·05	0·032
327	53·66	0·08	1175	90·95	0·028
444	61·83	0·062	1444	97·82	0·024

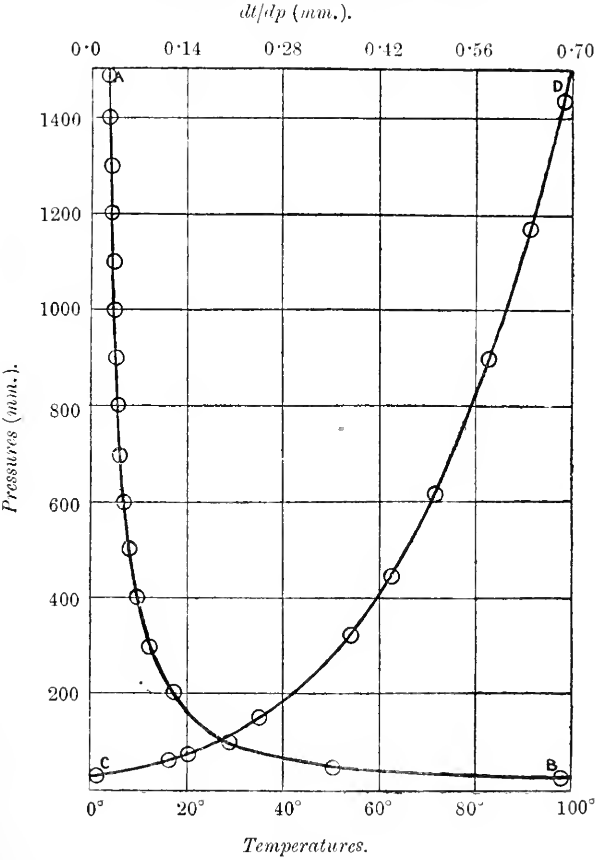
Anschütz thermometers were used; they had been compared with standard thermometers, and well known fixed points had also been used in calibrating them. The temperatures are reduced to the hydrogen scale in the latitude of Paris.

The vapour pressures and dt/dp plotted against the boiling points are represented in the two curves in Fig. 1.

A large-scale curve was drawn by plotting $\log p$ against the temperature. From this curve $\log p$ was read at a given temperature, and the corresponding pressure calculated. In this way the results given in column (*a*) of table II were found.

Fig. 1.

AB = dt/dp. CD = *vapour pressure curve.*



Another way in which the pressure at any temperature was found was by plotting the values of $\Delta \log p/\Delta t$ against the mean t. Then the vapour pressure at any temperature was calculated from the formula:

$$\log p_t = \log p_{t_1} + \frac{\Delta \log p}{\Delta t} \cdot (t - t_1).$$

The values are given in column (*b*) of table II; for convenience the values at 0° and 10° are added from table VI. The values obtained by Young and Thomas (Trans., 1893, **63**, 1216) are given in column (*e*).

Table II.

Temp.	From log. curve. (*a.*)	By log. difference from nearest experimental value. (*b.*)	Mean mm. (*c.*)	*dp/dt.* (*d.*)	Values (in mm.) of Young and Thomas. (*e.*)
0°			24·1	1·45	24·3
10			42·9	2·4	42·7
15	56·2	56·3	56·3	3·1	
20	72·6	73·0	72·8	3·7	72·8
30	118·5	119·0	118·7	5·7	118·7
40	186·2	186·7	186·4	8·0	186·2
50	282·5	282·6	282·5	11·4	282·2
60	415·4	414·8	415·1	15·7	415·4
70	596·5	595·7	596·1	20·8	596·3
80	832·8	833·6	833·2	27·1	832·7
90	1138·0	1140·0	1139·0	34·7	1130·0
100	1537·0	1535·0	1536·0	43·9	1515·0

The agreement with the results of Young and Thomas is very good, except at 90° and 100°, where the values for the pressure obtained by the authors exceeds the previous values by 9 mm. and 21 mm. respectively. Young and Thomas used the static method, which usually gives high values for the vapour pressure.

The authors carefully tested the point by doing three distillations, with the following results:

Table III.

Pressure in mm.	Boiling point.	Reduced to 1470 mm.
1471·7	98·49°	98·45°
1472·3	98·49	98·44
1470·7	98·46	98·44

These results correspond with a vapour pressure of 1535 mm. at 100° and a boiling point of 99·16° under a pressure of 1500 mm.

The value given in column (*c*) of table II was thus confirmed, proving that the values of Young and Thomas were low. In order to make further tests, the following curves were drawn: (*a*) p plotted against t; (*b*) $\log p$ against t; (*c*) first differences against mean t; (*d*) second differences against mean t. The high values of column *c* fell exactly on these curves, whilst there was no doubt that the values of Young and Thomas were off the curves, especially in the case of the last two curves, which tend to magnify any errors.

In the following table the boiling points of ethyl acetate at various pressures are given.

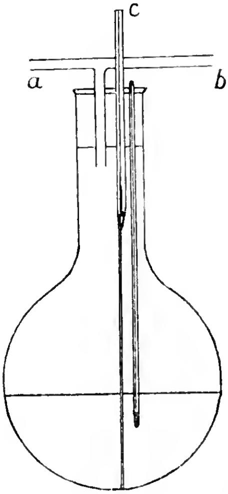
TABLE IV.

Pressure in mm.	Boiling point.	*dt/dp*.	Pressure in mm.	Boiling point.	*dt/dp*.
25	0·61°	0·68	700	74·72°	0·043
50	12·75	0·37	760	77·15	0·040
75	20·54	0·27	800	78·71	0·038
100	26·15	0·20	900	82·40	0·035
150	34·93	0·155	1000	85·70	0·0315
175	38·48	0·14	1100	88·77	0·0293
200	41·73	0·121	1200	91·65	0·028
300	51·44	0·086	1300	94·33	0·026
400	58·98	0·068	1400	96·82	0·0246
500	65·12	0·056	1500	99·16	0·0232
600	70·19	0·048			

II.—*Vapour Pressures below* 15°.

For low pressures the apparatus sketched in Fig. 2 was used.

FIG. 2.



The end (a) of the T-piece is joined to the manometer, and the end (b) to the manostat, air reservoir, and air pump. The thick-walled capillary (c) is drawn out to a long, very fine point, which presses against the bottom of the flask. The top of this capillary is joined to a Drechsel bottle containing concentrated sulphuric acid, so that only dry air enters the flask. The quantity of air required to promote steady boiling is very small, not more than 1 c.c. in thirty minutes, as the bubbles which enter through the fine capillary are extremely minute. The thermometer dips below the surface of the liquid. The flask rests on a thin layer of cotton-wool, and no artificial external heat is used.

When the pressure, as regulated by the manostat, had reached a constant value, the boiling point remained steady for an indefinite period. As soon as the pressure was altered the temperature adjusted itself with remarkable rapidity to a new constant value. With the room at 20° the temperature of the boiling liquid could be kept steadily at 0°, the deposit of dew forming a protective coating against the external heat.

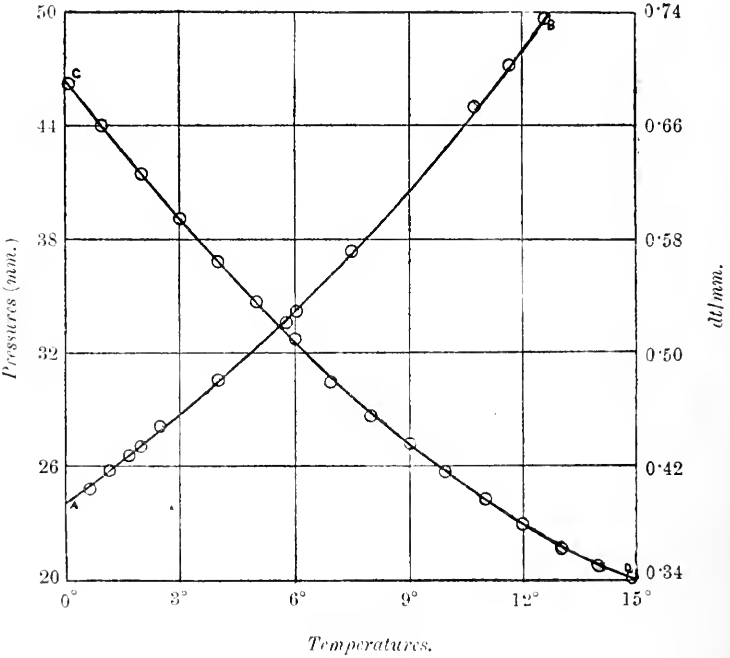
The experimental results are given in table V, and are represented on the curve in Fig. 3.

Table V.

Pressure in mm.	Boiling point.	Pressure in mm.	Boiling point.
24·9	0·60°	30·6	4·0°
25·7	1·15	33·4	5·7
26·6	1·60	34·0	6·05
26·9	1·80	37·3	7·5
27·0	1·95	45·0	10·7
27·2	2·00	47·2	11·6
28·2	2·5	50·0	12·7

Fig. 3.

AB = *vapour pressure curve.* CD = dt/dp.



The values in column (*a*) of table VI were read from this curve. The first differences were smoothed, giving the final values in column (*b*) and the values of dt/dp in column (*c*). The latter values are plotted against the temperature in Fig. 3.

TABLE VI.

Temp.	(*a.*) Vapour pressure from curve, in mm.	(*b.*) Smoothed value of pressure, in mm.	(*c.*) *dt*/*dp*, in mm.
0°	24·1	24·1	0·69
1	25·6	25·6	0·66
2	27·2	27·2	0·625
3	28·7	28·8	0·595
4	30·5	30·5	0·555
5	32·3	32·3	0·535
6	34·2	34·2	0·51
7	36·3	36·2	0·48
8	38·5	38·3	0·455
9	40·7	40·5	0·435
10	43·1	42·9	0·415
11	45·6	45·4	0·395
12	48·3	48·0	0·38
13	50·9	50·7	0·36
14	—	53·5	0·35
15	—	56·4	0·34

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CCLV.—*The Alkaline Condensations of Nitrohydrazo-compounds. Part III. Influence of ortho-Groups on Their Formation and Condensation.*

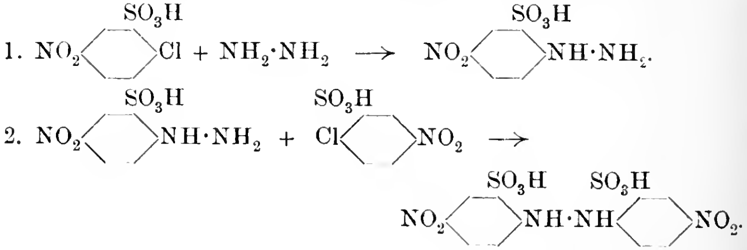
By ARTHUR GEORGE GREEN and FREDERICK MAURICE ROWE.

IT has been shown by Green and Stainton and by Green, Davies, and Horsfall (Trans., 1907, **91**, 2076) that the introduction of negative groups, such as the sulphonic and nitro-groups, in the ortho-position with respect to the methyl group in *p*-nitrotoluene greatly facilitates the stilbene condensation. In view of the analogy established in the earlier part of this investigation (Green and Bearder, Trans., 1911, **99**, 1960) between 4:4′-dinitroazobenzene and 4:4′-dinitrostilbene, both as to their formation and their reactions, it was to be anticipated that a similar increase of reactivity would be effected by introducing negative groups into the ortho-position of *p*-nitroaniline.

In order to test this assumption and at the same time to obtain the disulphonic acid of dinitroazobenzene, which compound was required as the starting point for preparing sulphonated derivatives of the products already described, we have submitted *p*-nitroaniline-

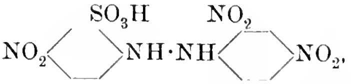
o-sulphonic acid to oxidation with sodium hypochlorite under the same conditions as were previously employed for preparing dinitroazobenzene from *p*-nitroaniline. Contrary to expectation, no reaction appeared to occur, the product remaining diazotisable and giving with "R-salt" the same colour as that given by the original *p*-nitroanilinesulphonic acid. The procedure was then modified in a number of ways, that is, by varying the temperature and other conditions, by adding a salt of copper, iron, nickel, or cobalt to serve as a catalyst, and by employing other oxidising agents, such as potassium permanganate and Caro's acid. In all cases the same negative result was obtained.

In view of this failure to obtain the dinitroazobenzenedisulphonic acid by direct oxidation, we then endeavoured to prepare the corresponding hydrazo-compound by condensing hydrazine with 2-chloro-5-nitrobenzenesulphonic acid, according to the following scheme:



Only the first of these two reactions occurred, and attempts to effect the second failed in every case. The only product which could be isolated from the mixture was *p*-nitrophenolsulphonic acid. An attempt to obtain the dinitroazobenzenedisulphonic acid by a similar condensation of the chloronitrobenzenesulphonic acid with an alkaline solution of hydroxylamine was also without result, and we were also unable to introduce the sulphonic groups by direct sulphonation of dinitroazobenzene.

In order further to investigate the nature of this remarkable resistance to the formation of compounds containing a sulphonic radicle in the ortho-position with respect to the basic nitrogen, we next attempted to prepare 4 : 2′ : 4′-trinitrohydrazobenzene-2-sulphonic acid,



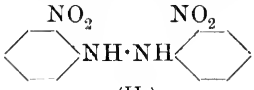
in which the ortho-position is occupied by a nitro-group in one nucleus, and by a sulphonic group in the other. The following mixtures were subjected to reaction under various conditions: (1) Molecular proportions of *p*-nitrophenylhydrazine-*o*-sulphonic acid and chlorodinitrobenzene, and (2) molecular proportions of

2:4-dinitrophenylhydrazine and 2-chloro-5-nitrobenzenesulphonic acid. The product of both reactions was again only *p*-nitrophenol-*o*-sulphonic acid, and no trace of a hydrazo-compound could be detected. Lastly, we attempted to prepare 4:4′-dinitrohydrazobenzene-2-monosulphonic acid,

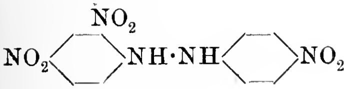
by acting with *p*-nitrophenylhydrazine on 2-chloro-5-nitrobenzenesulphonic acid; but although various experimental conditions were tried, we failed in this direction also to obtain a result.

In order to ascertain whether the inhibiting effect is exerted by other similarly situated electronegative groups, we next investigated the influence of the nitro-group, and for this purpose examined the conditions of formation of the following polynitrohydrazobenzenes:

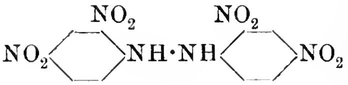
(I.)*



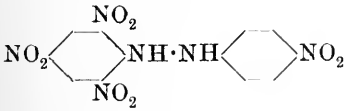
(II.)



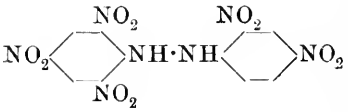
(III.)†



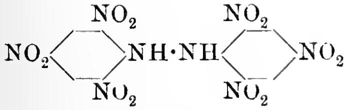
(IV.)



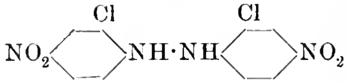
(V.)



(VI.)‡



(VII.)§



(VIII.)

Whilst by following the methods given by Werner and Stiasny, and by Leemann and Grandmougin, we were readily able to prepare the trinitro-, pentanitro-, and hexanitro-compounds (III, VI, and VII); and by treating picryl chloride with *p*-nitrophenylhydrazine we further succeeded in obtaining the previously unknown tetranitro-compound (V), we yet failed, by the application of similar methods, to obtain the symmetrical tetranitrohydrazobenzene (IV). Just as in the attempt to prepare dinitroazobenzenedisulphonic acid, the reaction between 4-chloro-1:3-di-

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* Lermontoff. † Werner and Stiasny, *Ber.*, 1900, **33**, 3277.

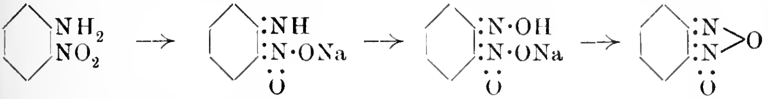
‡ Leemann and Grandmougin, *Ber.*, 1908, **41**, 1306.

§ *Ibid.*, 1906, **39**, 4384; 1908, **41**, 1295.

nitrobenzene and hydrazine stops half-way with the formation of the dinitrophenylhydrazine, and all endeavours to condense this compound with a further molecule of chlorodinitrobenzene, although carried out under a variety of conditions, proved abortive. As condensing agents, sodium acetate, potassium acetate, precipitated chalk, sodium carbonate, and sodium ethoxide were each in turn tried. Experiments were made with various solvents, for example, dilute alcohol, absolute alcohol, amyl alcohol, benzene, and xylene. The catalytic action of copper powder, cuprous chloride, and cuprous iodide was investigated, and, lastly, Werner and Stiasny's method of employing an excess of hydrazine without a solvent was also tried. In no case was there the least indication of the formation of tetranitrohydrazobenzene.

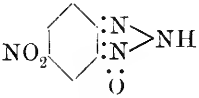
A similar resistance to the formation of the corresponding azo-compound is exhibited when dinitroaniline is submitted to oxidation with sodium hypochlorite in aqueous suspension or solution, and it was only when this oxidation was carried out with neutral hypochlorite in a non-ionising solvent (tetrachloroethane) that we finally succeeded in obtaining 2:4:2′:4′-tetranitroazobenzene, and from it by reduction the corresponding tetranitrohydrazobenzene. It is of interest to note also that the further nitration of 4:4′-dinitroazobenzene does not produce the tetranitro-compound, but gives instead under all conditions 2:4:4′-trinitroazoxybenzene, a substance which crystallises in yellow needles melting at 136°. On the other hand, we readily obtained the tetranitroazobenzene by further nitration of 2:2′-dinitroazobenzene, in which the resistant ortho-positions are already occupied.

A consideration of these facts clearly shows that the presence in the reacting amine or hydrazine of sulphonic or nitro-groups in the ortho-position with respect to the basic nitrogen exerts an impeding effect on condensation, although this impediment is counterbalanced when the more reactive picryl chloride is condensed with the hydrazine. From the fact that the reactivity of the hydrazine is not further diminished, but is rather increased, by the introduction of a second *o*-nitro-group, it is very improbable that we have to deal with sterical hindrance, and this is further supported by the consideration that in the stilbene series an exactly opposite action of negative ortho-groups has been established. We are therefore led to believe that the impeding effect is attributable to a tendency for ring condensation to occur between the *o*-nitro- or *o*-sulphonic group and the amino- or hydrazine group. This hypothesis receives strong support from a study of the action of oxidising agents on *o*-nitroaniline. Whilst *p*-nitroaniline is readily converted into 4:4′-dinitroazobenzene by oxidation with hypochlorites under all conditions, it was found that *o*-nitroaniline was only converted into 2:2′-dinitroazobenzene when submitted to oxidation with quite neutral sodium hypochlorite, preferably in alcoholic solution. When, on the other hand, an ordinary alkaline solution of sodium hypochlorite was employed and the oxidation effected in aqueous solution or suspension, no dinitroazobenzene was obtained, but there was formed instead an almost colourless, volatile, crystalline compound of peculiar odour, which proved on investigation (see following paper) to be identical with the product obtained by Zincke and Schwarz (*Annalen*, 1899, **307**, 28) by the spontaneous decomposition of *o*-nitrodiazobenzeneimide, and described by them as "*o*-dinitrosobenzene." The production of this compound suggests that in reality it is a furazan oxide (oxadiazol-oxide), and that its formation from *o*-nitroaniline occurs as follows:



Similar conditions hold good for 2:4-dinitroaniline, although here the alkaline oxidation is complicated by a displacement of the *p*-nitro-group. When oxidised with hypochlorite in alkaline solution a derivative of the above furazan oxide was produced, and it was only found possible to obtain the tetranitroazobenzene when the occurrence of quinonoid change was excluded by using neutralised hypochlorite and performing the oxidation in tetrachloroethane solution.

The impediment to the formation of *o*-nitrohydrazo-compounds may probably also be referred to ring condensations; thus in the interaction between chlorodinitrobenzene and dinitrophenylhydrazine the formation of the compound

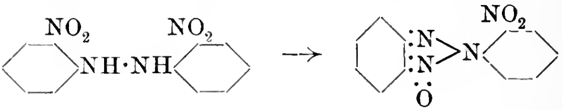


appears probable (compare Nietzki and Braunschweig, *Ber.*, 1894, **27**, 3381).

Moreover, the resistance to oxidation or condensation introduced by the presence of a sulphonic group in a similar position to the nitrogen is also capable of a similar interpretation if we assume the existence of analogously constituted rings in which the NO-group is replaced by SO_2H.

Such ring-formation would manifestly be impossible when the ortho-substituent is a halogen atom, and in order to study the influence of the latter we submitted *o*-chloro-*p*-nitroaniline to oxidation with hypochlorite in the ordinary manner. As was to be expected, the normal reaction occurred, although the yield of the dichlorodinitroazobenzene (probably on account of greater insolubility) was much smaller than that of dinitroazobenzene from *p*-nitroaniline.

With the object of investigating to what extent the action of the negative ortho-group influences the subsequent condensations, we have submitted the above-mentioned nitrohydrazo-compounds to the action of alkalis under various conditions. The results indicate that whilst all these compounds produce blue quinonoid salts, these salts are generally unstable when *o*-nitro-groups are present, and quickly undergo decolorisation. The most unstable in this respect of the compounds we have examined is 2 : 2′-dinitrohydrazobenzene, whilst the presence of a larger number of nitro-groups, as, for instance, in the hexanitro-compound, restores stability. The decolorisation is probably attributable to conversion into an azimino-oxide (compare Bamberger and Hübner, *Ber.*, 1903, **36**, 3822; Grandmougin and Guisan, *Ber.*, 1907, **40**, 4205):



In contrast to the above, 2 : 2′-dichloro-4 : 4′-dinitrohydrazobenzene, like 4 : 4′-dinitrohydrazobenzene, gives quinonoid salts of tolerable stability.

Experimental.

p-*Nitrophenylhydrazine*-o-*sulphonic Acid*, $C_6H_3(NO_2)(SO_3H)\cdot NH\cdot NH_2$.

A mixture of 25 grams of 2-chloro-5-nitrobenzenesulphonic acid, 13·7 grams of hydrazine sulphate, and 17·5 grams of crystallised sodium acetate dissolved in water was boiled with an inverted condenser for two hours. The *sodium* salt crystallises out on cooling, and was recrystallised from water. It forms easily soluble, orange-yellow needles. For analysis it was dried at 110°:

0·1974 gave 27·75 c.c. N_2 at 17° and 756 mm. N=16·59.
0·2314 ,, 0·2074 $BaSO_4$. S=12·31.
$C_6H_6O_5N_3SNa$ requires N=16·47; S=12·55 per cent.

2 : 4-*Dinitrophenylhydrazine*, $C_6H_3(NO_2)_2\cdot NH\cdot NH_2$.

This compound has been obtained by Purgotti (*Gazzetta*, 1894, **24**, i, 555) from chlorodinitrobenzene and hydrazine hydrate. It is readily prepared by the following method: Thirteen grams of hydrazine sulphate were stirred with a solution of 11¼ grams of potassium hydroxide in 50 c.c. of water. Alcohol (150 c.c.) was then added, and the potassium sulphate which separated was collected. The filtrate was then mixed with a hot concentrated alcoholic solution of $20\frac{1}{4}$ grams of chlorodinitrobenzene, followed immediately by a hot solution of $8\frac{1}{4}$ grams of crystallised sodium acetate in a little water. The mixture was boiled for five minutes, when the product separated in small, orange crystals, melting at 198°. The yield is nearly theoretical.

2 : 2′-*Dinitroazobenzene*, $NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NO_2$.

This compound has been described by Meigen and Normann (*Ber.*, 1900, **33**, 2715), but following the method given by these authors we were unable to obtain it. When ordinary alkaline hypochlorite is employed, the *o*-nitroaniline was either unattacked or was converted into the so-called "*o*-dinitrosobenzene." We finally succeeded in preparing the substance by excluding all free alkali, and thus preventing the tendency of the nitroaniline to pass into the quinonoid form.

Five grams of *o*-nitroaniline were dissolved in 100 c.c. of cold methyl alcohol, and to this solution was added a cold aqueous solution of sodium hypochlorite, which had been rendered just neutral to phenolphthalein paper by careful addition of dilute acetic acid. The mixture was well stirred, and the hypochlorite was employed in sufficient quantity to oxidise all the *o*-nitroaniline. The product which separated was collected, well washed with hot water, and crystallised from alcohol. It forms yellow needles, which melt at 197° (Meigen and Normann give 194—195°). It is readily soluble in acetone, benzene, or glacial acetic acid. The above authors give no analysis of the substance:

0·0735 gave 13·25 c.c. N_2 at 28·5° and 763 mm. N = 20·65.
$C_{12}H_8O_4N_4$ requires N = 20·59 per cent.

2 : 2′-*Dinitrohydrazobenzene*, $NO_2\cdot C_6H_4\cdot N_2H_2\cdot C_6H_4\cdot NO_2$.

Reduction was effected with colourless ammonium sulphide in the manner given by Green and Bearder for the 4 : 4′-isomeride (Trans., 1911, **99**, 1967). After boiling for about two minutes the mixture was diluted with water and allowed to cool. The precipitated product was separated, washed with dilute alcohol and with colourless ammonium sulphide, and then crystallised from alcohol or acetone. It crystallises from the latter in large, flat octahedra, which lose acetone on drying, and break up to a yellowish-brown, crystalline powder. It melts at 188°. When its acetone solution is added to alcoholic potassium hydroxide an exceedingly fugitive, violet-blue coloration is produced The instability of the quinonoid salt appears to be due to the occurrence of further condensation, and not to aerial oxidation:

0·0835 gave 14·95 c.c. N_2 at 28·5° and 763 mm. N=20·51.
$C_{12}H_{10}O_4N_4$ requires N=20·44 per cent.

2:4:6:4′-*Tetranitrohydrazobenzene*, $C_6H_2(NO_2)_3{\cdot}N_2H_2{\cdot}C_6H_4{\cdot}NO_2$.

A hot alcoholic solution of 3·15 grams of *p*-nitrophenylhydrazine was added to an alcoholic solution of 5 grams of picryl chloride, followed at once by 2 grams of precipitated chalk. After boiling for five minutes the product which separated was collected, extracted with dilute hydrochloric acid to remove impurities, washed with water, and finally recrystallised from glacial acetic acid with addition of a little water. The compound separates in fine, yellow prisms, melting at 214°. It dissolves in alkali hydroxides with a pure blue, and in concentrated sulphuric acid with an orange-red, colour. It is readily soluble in acetone or alcohol, but sparingly so in benzene or ether:

0·1178 gave 23·8 c.c. N_2 at 18° and 740 mm. N=23·26.
$C_{12}H_8O_8N_6$ requires N=23·08 per cent.

2:4:2′:4′-*Tetranitroazobenzene*, $C_6H_3(NO_2)_2{\cdot}N_2{\cdot}C_6H_3(NO_2)_2$.

Six grams of 2:4-dinitroaniline were dissolved in 90 c.c. of hot tetrachloroethane. A solution of sodium hypochlorite (about 5 per cent. active chlorine), carefully neutralised with dilute acetic acid, was then slowly added to the mixture kept at a temperature of about 70°, until further addition no longer produced a red coloration. The mixture was boiled until the tetrachloroethane had been expelled, and the granular residue was recrystallised from acetic acid or from a mixture of acetone and alcohol. 2:4:2′:4′-*Tetranitroazobenzene* forms pale orange-coloured needles, melting at 220°. It is very easily reduced to the hydrazo-compound, and therefore gives a blue coloration when sodium hydroxide alone is added to its alcoholic or acetone solution:

0·0837 gave 17 c.c. N_2 at 27·5° and 763 mm. N=23·92.
$C_{12}H_6O_8N_6$ requires N=23·20 per cent.

The same compound was also obtained by the further nitration of 2:2′-dinitroazobenzene by dissolving 1 gram of the latter in a mixture of 5 grams of concentrated sulphuric acid and 5 grams of fuming nitric acid. After remaining at the ordinary temperature for some time the mixture sets to a mass of fine orange needles. These were separated, washed with nitric acid, and recrystallised from a mixture of acetone and alcohol. The product melted at 220°, and was identical with that obtained by the preceding method.

2 : 4 : 2′ : 4′-*Tetranitrohydrazobenzene*, $C_6H_3(NO_2)_2{\cdot}N_2H_2{\cdot}C_6H_3(NO_2)_2$.

The employment of ammonium sulphide for reduction is unsuitable in this case, as, owing to the greater acidity of the product, the blue quinonoid salt is formed, and further condensation occurs. Good results are obtainable, however, by employing hydrogen sulphide as the reducing agent provided that the azo-compound is first converted into a fine precipitate by dissolving it in acetone and pouring the solution into water. The precipitate thus obtained from 2 grams of the azo-compound, washed free from acetone, was suspended in water, and a stream of hydrogen sulphide was passed through the mixture, which at the same time was slowly heated to the boiling point. When reduction was complete, the precipitate was collected, washed with cold ammonium sulphide to remove sulphur, then washed with water, and finally crystallised from a mixture of acetone and alcohol. From this solvent the product separates in small, yellow octahedra, melting at 250°. It is also soluble in glacial acetic acid, but insoluble in benzene. In concentrated sulphuric acid it dissolves with a yellow, and in aqueous sodium hydroxide with a pure blue, colour:

0·0963 gave 19·4 c.c. N_2 at 27·5° and 763 mm. N = 23·16.
$C_{12}H_8O_8N_6$ requires N = 23·08 per cent.

2 : 4 : 6 : 2′ : 4′-*Pentanitrohydrazobenzene*, $C_6H_2(NO_2)_3{\cdot}N_2H_2{\cdot}C_6H_3(NO_2)_2$.

Six grams of picryl chloride were dissolved in boiling alcohol, and a suspension of 4 grams of 2 : 4-dinitrophenylhydrazine in hot alcohol was added, followed by 2 grams of precipitated chalk. After boiling for two hours, the mixture was cooled, and the product which separated was washed with dilute hydrochloric acid and crystallised from acetic acid. The compound was also prepared by Leemann and Grandmougin's method (*loc. cit.*).

It forms slender, yellow needles, which melt and decompose at 228°. It is readily soluble in acetone, but only sparingly so in alcohol, ether, or benzene. It dissolves in concentrated sulphuric acid with an orange-yellow, and in alkali hydroxides with a pure blue, colour:

0·0605 gave 12·7 c.c. N_2 at 18° and 740 mm. N = 24·16.
$C_{12}H_7O_{10}N_7$ requires N = 23·96 per cent.

2 : 2′-*Dichloro*-4 : 4′-*dinitroazobenzene*, $NO_2{\cdot}C_6H_3Cl{\cdot}N_2{\cdot}C_6H_3Cl{\cdot}NO_2$.

Fifteen grams of *o*-chloro-*p*-nitroaniline (prepared by the chlorination of *p*-nitroaniline by Cassella's method, D.R.-P. 109189) was converted into a fine precipitate by dissolving in 80 per cent. acetic acid and pouring the solution into water. This precipitate, washed free from acid, was suspended in 1½ litres of cold water rendered alkaline with sodium hydroxide, and oxidised by the addition of sodium hypochlorite in excess. After stirring for six hours and allowing to remain overnight, the precipitate was collected, extracted with acetone to remove unaltered chloronitroaniline, and the residue recrystallised from solvent naphtha. The product forms brownish-red prisms, which melt at 274°. It is readily soluble in benzene, moderately so in glacial acetic acid, very sparingly so in acetone, and insoluble in alcohol:

0·1172 gave 16·8 c.c. N_2 at 17° and 756 mm. N=16·51.
0·1786 „ 0·1498 AgCl. Cl=20·76.
$C_{12}H_6O_4N_4Cl_2$ requires N=16·43; Cl=20·82 per cent.

2:2′-*Dichloro*-4:4′-*dinitrohydrazobenzene*,
$NO_2\cdot C_6H_3Cl\cdot N_2H_2\cdot C_6H_3Cl\cdot NO_2$.

The azo-compound was reduced with colourless ammonium sulphide in the manner employed by Green and Bearder for the reduction of 4:4′-dinitroazobenzene. The product crystallises from a mixture of alcohol and acetone in pale yellow, prismatic needles, melting at 214—215°. It is readily soluble in acetone, moderately so in glacial acetic acid, sparingly so in alcohol, and insoluble in benzene. It dissolves in concentrated sulphuric acid with an orange-yellow, and in aqueous alkali hydroxides with a pure blue, colour:

0·0701 gave 10 c.c. N_2 at 18° and 756 mm. N=16·38.
0·1760 „ 0·1464 AgCl. Cl=20·59.
$C_{12}H_8O_4N_4Cl_2$ requires N=16·32; Cl=20·7 per cent.

DEPARTMENT OF TINCTORIAL CHEMISTRY,
THE UNIVERSITY, LEEDS.

CCLVI.—*The Existence of Quinonoid Salts of* o-*Nitroamines and their Conversion into Oxadiazole Oxides.*

By ARTHUR GEORGE GREEN and FREDERICK MAURICE ROWE.

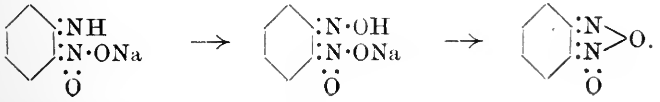
THE question of the existence of quinonoid forms of nitroamines has been the subject of frequent discussion and investigation. The proof afforded by Hantzsch of the existence of *aci*-salts of nitrophenols seems to render it not unlikely that in alkaline solution the nitroamines may also yield analogous *aci*-salts of the type

$C_6H_4{<}^{NH}_{NO\cdot OM'}$. In the ortho-series this view receives some support from the fact that *o*-nitroaniline dissolves in alcoholic potassium hydroxide with a deep reddish-orange, and 2:4-dinitroaniline with a bluish-red, colour. Attempts to decide this question by physical methods (Baly, Steward, and Edwards, Trans., 1906, **89**, 514; Baly, Tuck, and Marsden, *ibid.*, 1910, **97**, 580; Hantzsch, *Ber.*, 1910, **43**, 1669; Morgan and Clayton, Trans., 1911, **99**, 1945; Morgan, Jobling, and Barnett, this vol., p. 1209) have not led to definite conclusions, and further evidence of a chemical nature is therefore desirable.

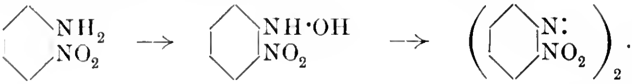
A recent observation made by Suida (*Chem. Zeit.*, 1912, **36**, 622) that the nitroanilines when dyed on wool cannot be diazotised by nitrous acid, would seem to indicate that the nitroamine is combined with the fibre in the form of a protein salt of a quinonoid nitronic acid, and the facts which follow also point unmistakably to the existence in the case of *o*-nitroaniline and other *o*-nitroamines of *aci*-quinonoid salts.

In the course of the previous investigation, in which it was observed that *o*-nitro-groups diminished the reactivity of basic nitrogen, we were led to examine the action of hypochlorites on *o*-nitroaniline. It was then found that when the oxidation was performed in warm aqueous solution with ordinary alkaline sodium hypochlorite almost the sole product was the so-called "dinitrosobenzene," and that the normal reaction only occurred when absolutely neutral conditions were maintained. The difference in the result is very striking when the oxidation is effected in both cases in cold methyl-alcoholic solution, using in one case completely neutral conditions, and in the other adding sufficient potassium hydroxide to render the solution a deep orange. In the first case only dinitroazobenzene is produced; in the second, "dinitrosobenzene" is obtained in theoretical yield, the orange colour disappearing as the reaction proceeds.

In view of the fact that "dinitrosobenzene" is undoubtedly a quinonoid compound (compare its conversion into *o*-benzoquinonedioxime by reduction, and its analogy to the so-called "glyoxime peroxide," "benzildioxime peroxide," and "camphordioxime peroxide"), and considering the improbability of a migration of oxygen from a nitro-group to the adjacent nitrogen atom, we are led to the conclusion that the reaction in alkaline solution takes place according to the scheme:



This is supported by the fact that in neutral solution the oxidation takes an entirely different and more normal course:

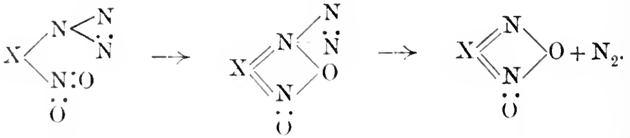


It follows, therefore, with great probability that in an alkaline solution the *aci*-salt of the quinonoid nitronic acid is present, whilst in neutral solution *o*-nitroaniline exists mainly in the benzenoid form.

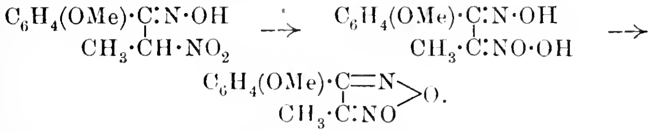
The identity of our product with the "dinitrosobenzene" obtained by Noelting and Kohn (*Chem. Zeit.*, 1894, **18**, 1905) and by Zincke and Schwarz (*Annalen*, 1899, **307**, 28) by decomposition of *o*-nitrodiazobenzeneimide, was established by its conversion into the corresponding dioxime and furazan. Other *o*-nitroamines when submitted to oxidation with hypochlorites in alkaline solution behave similarly, and the reaction affords a ready method of preparing compounds of this type; thus, from *m*-nitro-*p*-toluidine we have prepared the "dinitrosotoluene" obtained by Zincke and Schwarz from *m*-nitro-*p*-diazotolueneimide.

When, however, 2:4-dinitroaniline dissolved in methyl alcohol was submitted to similar treatment, there was obtained in place of the expected "*p*-nitrodinitrosobenzene" of Zincke and Schwarz a compound melting at 80°, which on investigation proved to be a chloromethoxy-derivative, $C_6H_2Cl(OMe)N_2O_2$. The oxidation, therefore, is accompanied in this case by a very remarkable replacement of the *p*-nitro-group by a methoxy-group followed by the introduction of a chlorine atom. The substitution of ethyl alcohol for methyl gave rise to the corresponding chloroethoxy-derivative, $C_6H_2Cl(OEt)N_2O_2$, but we failed to find conditions under which the nitro-group could be preserved intact.

The constitution of these compounds as benz*iso*oxadiazole (furazan) oxides,  $X{<}{\overset{N}{\underset{\underset{\ddot{O}}{N}}{}}}{>}O$, which is indicated by the new method of formation, also agrees well with their production from nitrodiazoimides, and does not necessitate a transference of an oxygen atom:



The furazan oxide constitution stands, moreover, in better accord with the properties of this class of compounds (for example, their stability to acids and resistance to reduction and oxidation) than the dioxime peroxide formula, $\mathrm{X}{<}\begin{matrix}\mathrm{N\cdot O}\\ \mathrm{N\cdot O}\end{matrix}$, advocated by Forster and Fierz (Trans., 1907, **91**, 1943). It may be noted also that in the fatty series, Wieland and Angeli (*Annalen*, 1903, **329**, 239) have described for the similarly constituted "glyoxime peroxides" a method of formation somewhat analogous to the above, which consists in treating the nitroketoximes with alkalis. Anetholenitrooxime, for example, reacts thus:

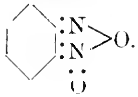


$$\begin{matrix}\mathrm{C_6H_4(OMe)\cdot C{:}N\cdot OH}\\ \mathrm{CH_3\cdot CH\cdot NO_2}\end{matrix} \longrightarrow \begin{matrix}\mathrm{C_6H_4(OMe)\cdot C{:}N\cdot OH}\\ \mathrm{CH_3\cdot C{:}NO\cdot OH}\end{matrix} \longrightarrow \begin{matrix}\mathrm{C_6H_4(OMe)\cdot C{=}N}\\ \mathrm{CH_3\cdot C{:}NO}\end{matrix}{>}\mathrm{O}.$$

Wieland and Semper (*Annalen*, 1908, **358**, 36) accordingly attribute to these aliphatic "glyoxime peroxides" a furazan oxide constitution similar to that which is here proposed for their aromatic analogues.

EXPERIMENTAL.

Benzisooxadiazole Oxide (Benzfurazan Oxide, "Dinitrosobenzene," or "o-Benzoquinonedioxime Peroxide"),

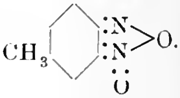


Ten grams of *o*-nitroaniline were dissolved in 150 c.c. of saturated alcoholic potassium hydroxide. A solution of sodium hypochlorite was then added in the cold with constant shaking until the crimson colour had entirely disappeared. The mixture was poured into an open dish and left to crystallise, when the product (9·5 grams) separated out in a nearly pure state. When crystallised from water or alcohol it forms white needles melting at 72°, as stated by Zincke and Schwarz. It is volatile with steam, and has a peculiar, pungent odour.

The compound can also be conveniently prepared by adding a solution of sodium hypochlorite to a hot aqueous solution of *o*-nitroaniline, rendered alkaline with sodium hydroxide, until the solution is nearly colourless. On cooling, the product crystallises in small, yellowish-white needles. (Found, N = 20·69. Calc., N = 20·58 per cent.)

o-Benzoquinonedioxime, $\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{N\cdot OH}\\ \mathrm{N\cdot OH}\end{matrix}$, was prepared by reducing the product of the previous reaction by means of alkaline hydroxylamine in the manner described by Zincke and Schwarz (*loc. cit.*). It crystallises from hot water or dilute alcohol in small, brownish-yellow needles, which melt and evolve gas at 145° (Zincke and Schwarz give 142°). It gives deep red solutions with alkalis, and dissolves with the same red colour in concentrated acids. It is interesting to note that the compound is a mordant dyestuff giving brown lakes with the oxides of chromium and copper, and a black lake with oxide of iron.

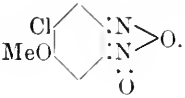
Benzisooxadiazole (*benzfurazan*),  $C_6H_4\langle\!\!\begin{smallmatrix}N\\N\end{smallmatrix}\!\!\rangle O$, was obtained by dissolving the dioxime in sodium hydroxide, and distilling it in a current of steam. The product, when recrystallised from alcohol, forms long, white needles, melting at 55° (as given by Zincke and Schwarz), readily soluble in most solvents, and very volatile.

5-Methylbenzisooxadiazole Oxide (*Tolufurazan Oxide*, "*Dinitrosotoluene*," *or* "*o-Toluquinonedioxime Peroxide*"), 

Ten grams of *m*-nitro-*p*-toluidine were dissolved in 200 c.c. of alcoholic potassium hydroxide, and a solution of sodium hypochlorite was added in the cold with constant shaking until the deep red colour had disappeared. The product separated as a pale yellow precipitate, which after crystallisation from dilute alcohol or hot water forms readily soluble, white needles, melting at 97° (Zincke and Schwarz give 96—97°).

3 : 4-*Toluquinonedioxime*,  was obtained by reduction of the preceding compound with alkaline hydroxylamine. It forms small, yellow needles, melting and decomposing at 128° (Zincke and Schwarz give 127—128°). It forms deep red solutions with alkalis or strong acids, and possesses mordant-dyeing properties similar to its lower homologue. (Found, N = 18·55. Calc., N = 18·43 per cent.)

5-Methylbenzisooxadiazole (*Tolufurazan*),  was obtained from the preceding substance by distillation of its sodium hydroxide solution in a current of steam. It separates from dilute alcohol in long, white needles, melting at 37° (as given by Zincke and Schwarz), which are readily soluble in solvents and very volatile. (Found, N = 20·91. Calc., N = 20·89 per cent.)

6-*Chloro*-5-*methoxybenz*isoo*xadiazole Oxide* (*Chloromethoxybenzfurazan Oxide*), 

Ten grams of 2:4-dinitroaniline were dissolved in 350 c.c. of methyl alcohol, and 75 c.c. of a concentrated methyl-alcoholic solution of potassium hydroxide were added. To the deep crimson solution warmed to 50° there was added, with constant shaking, sodium hypochlorite solution (containing 5 per cent. of active chlorine) until decolorisation occurred, and the colour was not restored by adding more alcoholic potassium hydroxide. The crystals which separated after some time were recrystallised from alcohol. The compound forms long, pale yellow needles, which melt at 80·5°. It is readily soluble in alcohol, acetic acid, or benzene, and insoluble in water.

Analysis demonstrated that the product is not the expected nitrobenzfurazan oxide, but that the oxidation is accompanied by a displacement of the second nitro-group by methoxyl and the introduction of a chlorine atom:

0·0859 gave 10·3 c.c. N_2 at 19° and 761 mm. N = 14·14.
0·2326 „ 0·1646 AgCl. Cl = 17·51.
0·3062 „ 0·3523 AgI. OMe = 15·18.
$C_7H_5O_3N_2Cl$ requires N = 13·96; Cl = 17·70; OMe = 15·46 per cent.

On complete reduction with zinc dust and alcoholic hydrochloric acid the product gave a base, the acetyl compound of which melted at 203°. This base was characterised as an ortho-diamine by its yielding an azimino-compound (m. p. 227°) and its condensation to a yellow glyoxaline with phenanthraquinone.

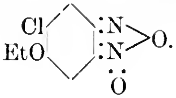
Chloromethoxy-o-*benzoquinonedioxime*, 

was obtained by reduction of an alcoholic solution of the preceding compound with alkaline hydroxylamine. The substance crystallises from dilute alcohol in small, brownish-yellow prisms, which melt at 152°. It is readily soluble in alcohol or acetic acid, but less so in water or benzene. In alkali hydroxides, carbonates, or acetates it dissolves with a deep red colour, and also gives similar-coloured solutions with strong acids. It has mordant dyeing properties:

0·0886 gave 10·6 c.c. N_2 at 18° and 757 mm. N = 14·09.
0·2062 „ 0·1467 AgCl. Cl = 17·60.
$C_7H_7O_3N_2Cl$ requires N = 13·82; Cl = 17·53 per cent.

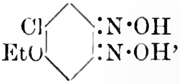
6 - *Chloro* - 5 - *methoxybenz*isoo*xadiazole* (*Chloromethoxybenzfurazan*),  was prepared from the dioxime by subjecting its alkali hydroxide solution to steam distillation. The oil which passed over crystallised on cooling, and was collected and recrystallised from alcohol. It forms slender, white needles, which melt at 76°, and are readily soluble in the usual solvents. It is volatile with steam:

0·0964 gave 12·5 c.c. N_2 at 18° and 757 mm. N=15·30.
0·2192 „ 0·1694 AgCl. Cl=19·13.
$C_7H_5O_2N_2Cl$ requires N=15·18; Cl=19·24 per cent.

6-*Chloro*-5-*ethoxybenz*isoo*xadiazole oxide* (*Chloroethoxybenzfurazan Oxide*), 

Ten grams of 2:4-dinitroaniline are dissolved in 600 c.c. of absolute ethyl alcohol at 50°, and mixed with 80 c.c. of concentrated alcoholic potassium hydroxide. The deep crimson-coloured mixture is then treated with sodium hypochlorite solution in the same way as for the methoxy-compound. The product which separates out on allowing the mixture to remain overnight is collected and crystallised from ethyl alcohol. It forms yellow, prismatic crystals, melting at 55°, which are readily soluble in alcohol, acetic acid, or benzene, but insoluble in water:

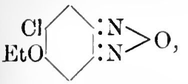
0·1610 gave 0·1068 AgCl. Cl=16·42.
0·3176 „ 0·3433 AgI. OEt=20·69.
$C_8H_7O_3N_2Cl$ requires Cl=16·55; OEt=20·97 per cent.

Chloroethoxy-o-*benzoquinonedioxime*,  was obtained by reduction of an alcoholic solution of the preceding compound with alkaline hydroxylamine. The substance crystallises from dilute alcohol in small, yellow needles, melting at 136°. It is readily soluble in alcohol or acetic acid, but less so in benzene or water.

Its properties are closely similar to those of the methoxy-compound:

0·2273 gave 0·1496 AgCl. Cl=16·29.
$C_8H_9O_3N_2Cl$ requires Cl=16·40 per cent.

6-*Chloro* - 5 - *ethoxybenz*isoo*xadiazole* (*chloroethoxybenzfurazan*),



, was prepared from the dioxime in the usual manner. It forms small, pale yellow prisms, melting at 48°, which are readily soluble in solvents and volatile with steam:

0·1694 gave 0·1213 AgCl. Cl = 17·71.
$C_8H_7O_2N_2Cl$ requires Cl = 17·88 per cent

The investigation is being continued.

Department of Tinctorial Chemistry,
The University, Leeds.

CCLVII.—*The Velocity of Reaction between Potassium Chloroacetate and Some Aliphatic Amines.*

By Tom Sidney Moore, Donald Bradley Somervell, and John Newton Derry.

A considerable number of experiments on the chemical dynamics of amines in non-aqueous solutions has been described in the literature, but no similar work on aqueous solutions appears so far to have been carried out. The present paper gives the results of experiments on the rate of reaction of ammonia, the three methylamines, the three ethylamines, and dipropylamine with potassium chloroacetate in aqueous solution at 25°.

In the case of ammonia, three successive reactions are possible:

(1) $NH_3 + CH_2Cl{\cdot}CO_2K = NH_2{\cdot}CH_2{\cdot}CO_2H + KCl.$

(2) $NH_2{\cdot}CH_2{\cdot}CO_2H + CH_2Cl{\cdot}CO_2K = CO_2K{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2H + HCl.$

(3) $CO_2K{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2H + CH_2Cl{\cdot}CO_2K = (CO_2K{\cdot}CH_2)_2N{\cdot}CH_2{\cdot}CO_2H + HCl.$

These reactions have been carried out on a preparative scale (Heintz, *Annalen*, 1864, **129**, 35; **132**, 1; 1866, **140**, 217; Kraut, Goldberg, and Kunz, *ibid.*, 1891, **266**, 292), and the basicities of the products appear to be those corresponding with the formulæ given above. For a primary amine two such reactions are possible, and for a secondary amine one only. Tertiary amines must act according to the equation:

(4)


$$NR_3 + CH_2Cl{\cdot}CO_2K = \begin{array}{l} CH_2{\cdot}NR_3 \\ | \quad\quad | \\ CO{-}O \end{array} + KCl.$$

If of the possible reactions the first one has a velocity considerably greater than the second, the latter may be neglected, and we get the differential equation $dx/dt = k(A-x)(B-x)$, where A and B are the original concentrations of the potassium chloroacetate and the amine. This on integration gives

$$\frac{1}{A-B}\log\frac{B}{A}\cdot\frac{A-x}{B-x}=kt.$$

Since the substituted glycine produced acts as a neutral substance towards lacmoid, x is determined as the loss in titre of the alkaline experimental solution in the time t.

If the second reaction takes place with a velocity comparable with that of the first reaction, the values of k given by the above formula will fall off with time. This effect was prominent in the case of methylamine only; it was not observed with ammonia, and with ethylamine, dimethylamine, and diethylamine there was a diminution in the value of k only towards the end of the experiment; it was not observed at all with dipropylamine. It must, however, be mentioned that in the case of ammonia, where the reaction is very slow, the experiments were not carried far enough to obtain trustworthy evidence as to the occurrence or non-occurrence of consecutive reactions.

In the case of methylamine, approximate values of the two velocity-constants involved (denoted by k and k') were obtained as follows. When the amount of the potassium salt of methyliminodiacetic acid, $CO_2K\cdot CH_2\cdot NMe\cdot CH_2\cdot CO_2K$, produced is still small with regard to the amount of methylglycine in the solution, that is, at the beginning of the experiment, the equation:

$$\frac{1}{A-aB}\log\frac{aB}{A}\cdot\frac{A-x}{aB-x}=(k+k')t$$

holds, where $a = k/(k+k')$. The results of the application of this formula to the first few measurements of methylamine are given on p. 2465.

In addition to the reactions already mentioned, another is taking place in all solutions, namely, the formation of potassium glycollate by the action of the hydroxyl ions necessarily present:

$$(5)\quad CH_2Cl\cdot CO_2' + OH' = OH\cdot CH_2\cdot CO_2' + Cl'.$$

The velocity of this reaction has been measured by Senter (Trans., 1907, **91**, 461) at 48·5° and 102°, for which temperatures the velocity-constants in the presence of potassium chloride (compare p. 2464) are 0·0011 and 0·23 respectively. From these numbers it appears that at 25° the constant of this reaction is 0·0003, which, when multiplied by 2·72 to make it comparable with our numbers which remain as common logarithms, becomes 0·00082.

This is of the same order as our constants for ammonia and triethylamine, the smallest of the series, but since the concentration of hydroxyl ions present in the solutions of bases so weak as aliphatic amines is very small compared with the total concentration of base (for which, naturally, our constants are calculated), it is clear that the amount of potassium chloroacetate undergoing hydrolysis must be very much smaller than the amount reacting with the amine according to equations 1, 2, 3, and 4. If any further proof that reaction (5) is comparatively so slow as to be negligible is needed, it is supplied in the fact that our velocity-constants bear no relation to the concentration of hydroxyl ion in solution, being, for example, very small for triethylamine, which has one of the largest apparent ionisation constants (Moore and Winmill, this vol., p. 1660).

The following are the values of the constants found:

Ammonia	0·00038	Diethylamine	0·0030
Methylamine	0·0069	Dipropylamine	0·0020
Ethylamine	0·0042	Trimethylamine	0·035
Dimethylamine	0·025	Triethylamine	0·00045

From this it appears that the velocity falls with increase of molecular weight among amines of the same type. Taking ratios, we find that methylamine reacts 1·6 times as quickly as ethylamine, dimethylamine 8·3 times as quickly as diethylamine, and trimethylamine 78 times as quickly as triethylamine. The effect of the larger groups thus increases with their number, as the prevailing theory of stereochemistry would lead us to expect. The decrease in the constant from diethylamine to dipropylamine (ratio = 1·5) is very nearly the same as the decrease from dimethylamine to diethylamine (ratio = 1·6). It is noticeable that the three methylamines have the largest constants, and that whereas the substitution of one ethyl group for two methyl groups diminishes the constant, the substitution of two propyl groups for three ethyl groups increases it considerably.

The results most readily comparable with these are those given by N. Menschutkin (*Zeitsch. physikal. Chem.*, 1895, **17**, 193) for the rate of reaction of amines with alkyl haloids in benzene solution at 100°, but before we proceed to the comparison it is necessary to point out some discrepancies in Menschutkin's paper. Since the solvent is benzene, the hydrobromic acid produced according to the equation

$$RNH_2 + Alk{\cdot}Br = R{\cdot}NH{\cdot}Alk + HBr$$

combines with amine to produce an insoluble hydrobromide. Three cases are therefore to be distinguished, namely, (1) when the precipitated salt is the hydrobromide of the amine formed in the reaction, (2) when it is the hydrobromide of the original amine, and

(3) when it is a mixture of the two. Menschutkin, by analysis of the precipitated hydrobromides, proved that all three cases occur.

The tables in Menschutkin's paper all give values of Ak calculated from the equation $Ak = \frac{1}{t}\log\frac{A - x/2}{A - x}$, where A is the original concentration of the alkyl haloid, the original concentration of the amine being $2A$, and A being approximately the same for all experiments. This equation is correct for the first case, but in the second should be replaced by $Ak = \frac{1}{2t}\frac{x}{A - x}$, corresponding with the differential equation $dx/dt = k(2A - 2x)(A - x)$.

Applying this equation to the cases where Menschutkin proved that the precipitated salt is the hydrobromide of the original amine (case 2 above), we find that the values of Ak then obtained are much less nearly constant than when Menschutkin's formula is used. For ammonia and allyl bromide the results are:

t.	$\frac{1}{t}\log_e\frac{A - x/2}{A - x}$.	$\frac{1}{2t}\frac{x}{A - x}$.
20	0·035	0·041
30	0·038	0·053
40	0·041	0·074
60	0·037	0·295

and in other examples of case 2 the results are very similar; thus the first formula, which here has no theoretical foundation, agrees with the results, whilst the correct theoretical formula does not. It is hoped that further work on the subject may be carried out in this laboratory for the purpose of finding the cause of this discrepancy.

In the meantime there is no reason to doubt that the numbers given by Menschutkin are accurate enough to enable us to write down the amines in the order of the magnitude of their velocity-constants. The numbers in the first four columns of the following table give the relative values of these constants for the reaction of the amine opposite which they are written with the alkyl bromide at the head of the column. The last column gives the values we have found for the reaction with potassium chloroacetate.

	CH_3Br.	C_2H_5Br.	C_3H_5Br.	C_3H_7Br.	$CH_2Cl\cdot CO_2K$.
$(CH_3)_2NH$	60,000	1530	34,300	—	0·025
$(CH_3)_3N$	47,400	1050	30,800	—	0·035
$CH_3\cdot NH_2$	31,900	490	8,300	—	0·0069
$C_2H_5\cdot NH_2$........	19,400	210	3,800	15	0·0042
$(C_2H_5)_2NH$	16,900	182	—	—	0·0030
$(C_3H_7)_2NH$	10,300	101	2,900	21	0·0020
NH_3	5,500	124	1,400	44	0·00038
$(C_2H_5)_3N$	5,400	30	760	—	0·00045

In the case of methyl bromide the constants are in descending order; for allyl bromide the order is the same; for ethyl bromide and for propyl bromide the order is the same, except that dipropylamine and ammonia are interchanged. The constants for potassium chloroacetate show, in general, the same order, the exceptions being di- and tri-methylamine, which have interchanged their positions, and ammonia and triethylamine, which again are interchanged, but which in this case, as with methyl bromide, give constants of nearly the same magnitude. At 51·2° Menschutkin found that trimethylamine reacts with methyl bromide more quickly than does dimethylamine.

The general agreement between the two sets of results is all the more remarkable, since the experimental conditions—100° in benzene solution on the one hand, and 25° in aqueous solution on the other—are so different.

The conclusion one would naturally draw from this coincidence is that the mechanism of the reaction is the same in the two media; and since in benzene the amines are present as such, and in water are present partly as amine, partly as amine hydroxide, and partly as ions, the conclusion follows that in aqueous solution it is the unhydrated amine that is active. Before this conclusion can be drawn, however, a correction must be applied to the reaction-constants we have found, for these have been calculated as if the whole of the amine were active. If k_2 is the hydration-constant of the amine, then neglecting the ionised part which is always very small, the fraction of amine present as such is $1/1+k_2$, and the fraction present as hydroxide is $k_2/(1+k_2)$. If the unhydrated amine is the active part in the reaction under consideration, the values of the reaction-constant must be multiplied by $(1+k_2)$ before they are comparable with one another, and the corresponding factor if the hydrated part is active is $(1+k_2)/k_2$.

The values obtained are as follows:

	Velocity-constant × $(1+k_2)$.	Velocity-constant × $(1+k_2)/k_2$.
$(CH_3)_2NH$	0·036	0·078
$(CH_3)_3N$	0·098	0·054
$CH_3·NH_2$	0·112	0·0073
$C_2H_5·NH_2$	0·014	0·0060
$(C_2H_5)_2NH$	Large	0·0030
$(C_3H_7)_2NH$	,,	0·0020
NH_3	0·00081	0·00072
$(C_2H_5)_3N$	0·00095	0·00086

Thus the numbers obtained on the hypothesis that the active part in our experiments is the unhydrated amine are no longer even approximately in the same order as Menschutkin's; whereas on the alternative hypothesis the order is the same as Menschutkin's except for ammonia and triethylamine. What this may mean is not clear, for analogy would be expected to occur, if at all, between Menschutkin's numbers and the first column, for both sets of numbers refer to reactions of simple amines; there seems no obvious reason why the numbers of the second column, which give the rates of reaction of amine hydroxides, should show any kind of analogy to Menschutkin's.

EXPERIMENTAL.

The method of experiment was the following: A solution of chloroacetic acid of strength varying in different experiments was made up, and its concentration determined by titration. A suitable volume of this solution was measured into a boro-silicate flask, and to it was added a weighed quantity of the pure hydrochloride of the amine to be examined. Potassium hydroxide was then added in quantity not quite sufficient to neutralise the chloroacetic acid and to liberate the amine from the hydrochloride, and the solution then made up quickly to a known volume and put in the thermostat at 25°. The concentration of the amine was calculated from the difference between the total amount of potassium hydroxide added and the amount necessary to neutralise the chloroacetic acid.

The progress of the reaction was followed by taking samples from time to time, which were each added immediately to 10 c.c. of *N*-acid, the excess of acid being then titrated with *N*/10-alkali in the presence of lacmoid. All the measuring vessels were calibrated before use.

From the method of making up the experimental solutions it will be seen that in every case potassium chloride is present, its concentration being equal to that of the amine. Since from Senter's results on the reaction between chloroacetic acid and hydroxyl ions (*loc. cit.*) it appeared that neutral salts have an effect on the velocity of the reaction varying with their concentration, it is possible that such an effect occurs with the reactions we have investigated, and that our constants are not strictly comparable with one another. From the fact, however, that different experiments with the same base showed no variation of the constant with initial concentration, we conclude that this effect, if present, is very small. Further, in the fourth experiment with ammonia excess of potassium chloride was added to the reaction mixture, with very little effect on the constant.

Ammonia.

(1) A = 0·7934; B = 0·2492.

t (minutes).	x.	k.
58·8	0·0099	0·00038
108·0	0·0175	0·00037
145·5	0·0236	0·00038
178·0	0·0297	0·00040
220·0	0·0353	0·00039
257·0	0·0406	0·00039
	Mean	0·00038

Ten values of k ranging between 0·00036 and 0·00040 were measured in all.

(2) A = 0·472; B = 0·902.

Eight values of k ranging between 0·00036 and 0·00040. Mean, 0·00038.

(3) A = 0·491; B = 0·5142.

Twelve values of k ranging from 0·00035 to 0·00039. Mean = 0·00037.

(4) A = 0·8266; B = 0·2507.

Enough potassium chloride was added to make the solution 0·2N. Since the normality of the potassium chloride produced from the amine hydrochloride is 0·251, the concentration of the potassium chloride is here roughly double that of the amine, whilst in all other experiments they are equal.

Eight values of k ranging from 0·00038 to 0·00041. Mean, 0·00039.

Methylamine.—A = 0·819; B = 0·1697.

Here the correction referred to on p. 2460 was applied. It was found that the value of $k + k'$ was most nearly constant for the first few readings when $a = k/(k+k')$ was made equal to 0·8.

t.	x.	k (without correction).	$k+k'$.
28·3	0·0482	0·0065	0·0085
44·8	0·0680	0·0064	0·0086
65·5	0·0859	0·0060	0·0086
102·0	0·0984	0·0049	0·0072
		Mean	0·0086

Therefore $k = 0·0069$
$k' = 0·0017$

This experiment thus indicates that in the case of methylamine a consecutive reaction occurs, but the relative values of the velocity-constants found for the two reactions need verification by further experiment.

Ethylamine.

A = 0·5483; B = 0·3793.

t.	*x.*	*k.*
11·8	0·0226	0·0042*
24·3	0·0431	0·0041*
47·0	0·0785	0·0042*
30 5	0·1073	0·0042*
106·5	0·1405	0·0040
150·8	0·1696	0·0038
180 0	0·1879	0·0038
271·0	0·2266	0·0036

* Mean 0·0042

Dimethylamine.

(1) A = 0·0692; B = 0·7749.

t.	*x.*	*k.*
19·3	0·0371	0·023
39·7	0·0565	0·025
59·0	0·0644	0·027
136·0	0·0689	0·025

Mean = 0·025

(2) A = 0·348; B = 0·2303.

t.	*x.*	*k.*
7·5	0·0305	0·025*
17·5	0·0680	0·025*
28·0	0·0900	0·026*
37·8	0·1029	0·024*
48·5	0·1139	0·022
60·5	0·1212	0·020
116·5	0·1435	0·014

* Mean = 0·025

Diethylamine.

(1) A = 0·0957; B = 0·2915.

t.	*x.*	*k.*
44·5	0·0092	0 0034
98·5	0·0170	0·0030
165·5	0·0257	0·0029
199·0	0·0302	0·0030

Mean 0·0030

(2) A = 0·1193; B = 0·2101.

t.	*x.*	*k.*
56·3	0·0125	0·0038
96·8	0·0156	0·0031
130·8	0·0206	0·0032
187·7	0·0261	0·0029

Mean 0·0031

Two other experiments were made with different values of A and B; both gave values for *k* near 0·0030 at the beginning, but lower values later in the experiment.

Dipropylamine.

(1) A = 0·471; B = 0·0567.

t.	*x.*	*k.*
27·0	0·0054	0·0021
53·0	0·0063	0·0021
107·5	0·0113	0·0019
156·0	0·0160	0·0020

Mean 0·0020

(2) A = 0·5253; B = 0·1508.

t.	*x.*	*k.*
12·3	0·0049	0·0022
25·0	0·0129	0 0022
43·8	0·0161	0·0021
76·5	0·0258	0·0021
107·5	0·0321	0·0019
141·0	0·0429	0·0021
189 0	0·0508	0·0019

Mean 0·002

Trimethylamine.

A=0·3195; B=0·0446.

t.	*x.*	*k.*
20	0·0166	0·033
33·5	0·0255	0·036
46·8	0·0308	0·036
63·5	0·0353	0·036
83·0	0·0379	0·035
98·8	0·0393	0·032
	Mean	0·035

Triethylamine.

A=0·5553; B=0·2503.

t.	*x.*	*k.*
17·7	0·0024	0·00049
57·5	0·0080	0·00044
118·3	0·0150	0·00041
191·5	0·0244	0·00043
225·0	0·0299	0·00046
302·0	0·0395	0·00046
399·0	0·0475	0·00043
	Mean	0·00045

The values found above are tabulated on p. 2461.

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CCLVIII.—*Properties of Mixtures of Ethyl Alcohol, Carbon Tetrachloride, and Water.*

By THOMAS HENRY HILL.

THE following research was undertaken with the object of determining whether mixtures of constant boiling point were afforded by the first two components and by the three taken together. As these mixtures were found to exist, their compositions were determined by the middle-point distillation method (S. Young, "Fractional Distillation," Ch. XVI), and in the case of the alcohol–carbon tetrachloride mixture, by means of a density curve. The composition of the ternary mixture as thus obtained was checked by extracting and weighing the carbon tetrachloride and determining the density of the alcoholic aqueous residue. The carbon tetrachloride was purified by distillation over phosphoric oxide through a three-section Young evaporator still-head, and the density of the product determined to be $D_{0^\circ}^{0^\circ}$ 1·63224, although in part of the work samples with slightly lower density were employed. The alcohol was obtained anhydrous by distillation with a twelve-section Young and Thomas dephlegmator. Throughout the paper boiling points are corrected to normal pressure, and weighings in density determinations corrected to weight in a vacuum. The alcohol–carbon tetrachloride mixture, boiling constantly at 65·2°, was found to contain 16·05 per cent. of alcohol as calculated from its density D 1·40178. There is no alteration in volume on mixing the components in these proportions. The distillation method with carbon tetrachloride in excess gives the value 16·4 per cent. of alcohol. With alcohol in excess the agreement is not so good, 15·3 per cent. being arrived at in this way. This behaviour is similar to that of allyl alcohol and benzene (Wallace and Atkins, this vol., p. 1958), poor results being obtained in this case also when alcohol is the residual liquid.

The ternary mixture, carbon tetrachloride, alcohol, water, boils constantly at 61·8°, and has the following composition, as determined by distillation: carbon tetrachloride 86·3, ethyl alcohol 10·3, and water 3·4 per cent. By the extraction method it was found to consist of carbon tetrachloride 86·0, alcohol 9·7, and water 4·3 per cent.

EXPERIMENTAL.

Density Determinations.

Employing Perkin's modification of the Sprengel tube, samples of carbon tetrachloride obtained from Kahlbaum and purified as described gave the following values: D^0_0 1·63152, 1·63160, 1·63173, 1·63174, 1·63224. It is evident that only the last measurement denotes an anhydrous product.

On redistilling a large volume of the alcohol–carbon tetrachloride mixture of constant boiling point, its density was found to be D^0_0 1·40178. Weighed quantities of the two liquids were then mixed, and the density of the mixture determined in each case; the theoretical density was calculated by the usual formula. The results are recorded below:

Alcohol per cent.	D^0_0 calc.	D^0_0 found.	Difference.
16·053	1·40135	1·40006	+ 0·00129
16·059	1·40128	1·40141	− 0·00013
16·173	1·39989	1·39962	+ 0·00027
16·050	1·40139	1·40234	− 0·00095
16·046	1·40144	1·40142	+ 0·00002
		Mean	+ 0·00010

In the first and fourth determinations, where the greatest divergence exists between calculated and found values, it is to be noted that the mixtures were not made as rapidly as usual, as one component had to be added in two portions, thus increasing loss by evaporation. Consequently, it seems fair to conclude that there is no volume change on mixing the two liquids.

Since this is so, it is permissible to calculate the composition of the mixture of constant boiling point from its density. Taking D^0_0 0·80625 for ethyl alcohol and D^0_0 1·63165 for the carbon tetrachloride employed, the mixture was found to contain 16·05 per cent. of the former component.

Distillation of Ethyl Alcohol and Carbon Tetrachloride.

Mixtures as tabulated below were distilled through a three-section Young evaporator still-head, and the composition of the mixture of constant boiling point was calculated by the middle-point method:

Mixture taken.	Carbon tetrachloride in excess.		Alcohol in excess.			
	I.	II.	III.	IV.	V.	VI.
Alcohol	13·7	16·00	40·5	50·17	50·17	58·8
Carbon tetrachloride	103·1	102·81	50·9	106·51	106·51	175·7
Composition of mixture of constant boiling point, alcohol per cent.	16·6	16·2	14·5	15·2	15·5	15·2

As before noticed, agreement with the results calculated from the density is better when carbon tetrachloride is in excess. The effect of using a small amount of liquid is apparent in No. III. No. V was obtained by redistilling No. IV up to the boiling point of alcohol. This second distillation improves the result. No. VI was distilled through an eighteen-section Young and Thomas dephlegmator, but the separation even with it is not sharp.

Distillation of Ethyl Alcohol, Carbon Tetrachloride, and Water.

A five-section Young evaporator still-head was employed in the distillation of the first two of the following mixtures. Fractions were collected up to and between the various middle points. The remainder of the mixtures were distilled through the eighteen-section dephlegmator mentioned before.

Mixture taken.	I.	II.	III.	IV.	V.	VI.	Mean.
Alcohol	30·6	17·7	6·5	31·7	9·5	56·3	—
Carbon tetrachloride	90·5	179·6	163·1	77·8	137·5	129·0	—
Water	2·2	4·2	3·7	13·5	38·7	26·7	—
Composition of mixture of constant boiling point per cent. alcohol	10·5	10·1	10·4	9·8	10·5	9·8	10·3
Carbon tetrachloride	86·0	86·7	85·0	88·7	87·3	86·5	86·3
Water	3·5	3·2	4·6	1·5	2·2	3·7	3·4
Residual liquid	alcohol	carbon tetrachloride	carbon tetrachloride	water	water	water	

In taking the mean, the results of No. IV were omitted, as, owing to the smaller volume of liquid distilled, they were less accurate in this case.

Analysis of the Ternary Mixture of Constant Boiling Point.

A large amount of the mixture was slowly distilled through the eighteen-section dephlegmator, more than 300 c.c. of liquid of constant boiling point being thus obtained. The whole was weighed, and the carbon tetrachloride allowed to separate after addition of water. The latter was poured into a tared flask, having previously been repeatedly extracted with water to remove alcohol. The washings were subsequently distilled. The first fraction contained all the carbon tetrachloride. This separated after some time, and was added to that previously obtained, the total tetrachloride being then weighed. The washings were again distilled, up to the boiling point of water; the alcohol was, of course, all in the distillate. The composition of the latter was then ascertained from its density. Accordingly the composition of the mixture of constant boiling point could be calculated. Two analyses gave 86·3 and 85·7 per cent. of carbon tetrachloride; the latter analysis also gave the values 9·7 per cent. for alcohol and 4·6 per cent. for water.

It is clear from this work that distillation of suitable proportions of ethyl alcohol and carbon tetrachloride furnishes a means of obtaining anhydrous ethyl alcohol, but the process is not as economical as distillation with benzene as described by S. Young.

The inception of this work was due to the suggestion of Prof. Sydney Young, to whom I am indebted for constant advice throughout and for the use of apparatus.

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CCLIX.—*Position-Isomerism and Optical Activity: Halogen Derivatives of Methyl Dibenzoyltartrate.*

By Percy Faraday Frankland, Sidney Raymond Carter, and Ernest Bryan Adams.

The present paper forms a continuation of an inquiry into the relationship existing between optical activity and position-isomerism. The problem has already been attacked in a number of different ways, notably by a study of the benzoyl and toluoyl derivatives of several active hydroxy-esters. The rotatory properties of the three isomeric methyl dichlorobenzoyltartrates, and their bromine and iodine analogues, which are described in this paper, have an additional value from the fact that the benzoyl and toluoyl derivatives have already been investigated (Frankland and Wharton, Trans., 1896, **69**, 1309, 1583). A study of the rotatory powers of the latter compounds led to the application of Guye's lever-arm principle to benzene derivatives, and although this principle may not be capable of general application (compare this vol., p. 666), it is instructive to consider the data obtained for the halogen derivatives in this light.

The following table gives the values of the molecular rotations at 100° for the compounds concerned:

$[M]_D^{100°}$

Methyl dibenzoyl-tartrate.*		Methyl ditoluoyl-tartrates.*	Halogen derivatives of methyl dibenzoyltartrate.		
			Cl.	Br.	I.
—	ortho	−282°†	−212°	−176°	−105°
−280°	meta	327	352	376	431
—	para	426	445	500	[606] ‡

* Frankland and Wharton (*loc. cit.*).

† Above its melting point, 135·5°, the benzoyl derivative has a higher rotation than that of the *o*-toluoyl compound (see diagram, p. 2473).

‡ This compound has not yet been obtained crystalline and is, therefore, of doubtful purity; further purification would, however, probably raise this figure.

It will be seen that the halogens exert the same influence on the rotatory power of methyl dibenzoyltartrate as the methyl group in the toluoyl radicle, but in a greater degree. An increase in the weight of a substituent in the para- or meta-position has the effect of increasing the rotation. On the other hand, the tendency of the *o*-toluoyl group to depress the rotation of methyl dibenzoyltartrate becomes much more pronounced when the methyl group is replaced by a heavier halogen atom.

In each set of isomerides the usual order in rotatory power is maintained, namely, para>meta>ortho.

In this connexion it is interesting to compare the available data concerning other series containing a halogen-substituted benzene ring:

Tartaric Dianilides.

Rotation in Pyridine Solution $[M]_D^{20°}$.

Anilide.		Toluidide.	Chloroanilide.	Bromoanilide.	Iodoanilide.
—	ortho	+667°	+709°	+652°	—
+739°	meta	+730	+824	+867	+888°
—	para	+793	+838	+886	—

Frankland and Twiss, Trans, 1910, **97**, 155.

Menthyl Esters.

	Toluate.*	Fluoro-benzoate.†	Chloro-benzoate.‡	Bromo-benzoate.§	Iodo-benzoate.
ortho $[M]_D^{20}$ ...	$-231{\cdot}0°$	$-194{\cdot}5°$	$-195°$	$-205{\cdot}3°$	$-237°$
meta $[M]_D^{20°}$ ...	$-240{\cdot}0$	$-236{\cdot}0$	$-236{\cdot}9$	$-238{\cdot}7$	-237
para $[M]_D^{20°}$ ...	$-246{\cdot}5$	$-239{\cdot}0$	$-237{\cdot}3$	$-238{\cdot}8$	-237
ortho $[M]_D^{100°}$ ...	$-223{\cdot}0$	$-188{\cdot}5$	—	—	-236
meta $[M]_D^{100°}$ ...	$-234{\cdot}5$	$-229{\cdot}0$	—	—	$-233{\cdot}5$
para $[M]_D^{100°}$ ...	$-237{\cdot}0$	$-230{\cdot}0$	—	—	$-224{\cdot}0$

Menthyl benzoate * $[M]_D^{20°}$ $-239°$, $[M]_D^{100°}$ $-232{\cdot}7°$.

* Cohen and Dudley, Trans., 1910, **97**, 1732.
† Cohen, Trans., 1911, **99**, 1058.
‡ Cohen and Briggs, 1903, **83**, 1213.
§ Tschugaeff, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 606.

Acyl-d-*carvoximes.**

$[M]_D$ in chloroform solution (9—10 per cent.).			$[M]_D$ in chloroform solution (5·5 per cent.).
Benzoyl.		Toluoyl.	Bromobenzoyl.
—	ortho	$+76{\cdot}64°$	$+90{\cdot}34°$
$+71{\cdot}66°$	meta	$+76{\cdot}01°$	$63{\cdot}48$
—	para	$+66{\cdot}34$	$51{\cdot}85$

* *d*-Carvoxime, $[M]_D$ $+65{\cdot}37$, in alcoholic solution (9·8 per cent.). Goldschmidt and Freund, *Zeitsch. physikal. Chem.*, 1894, **14**, 394.

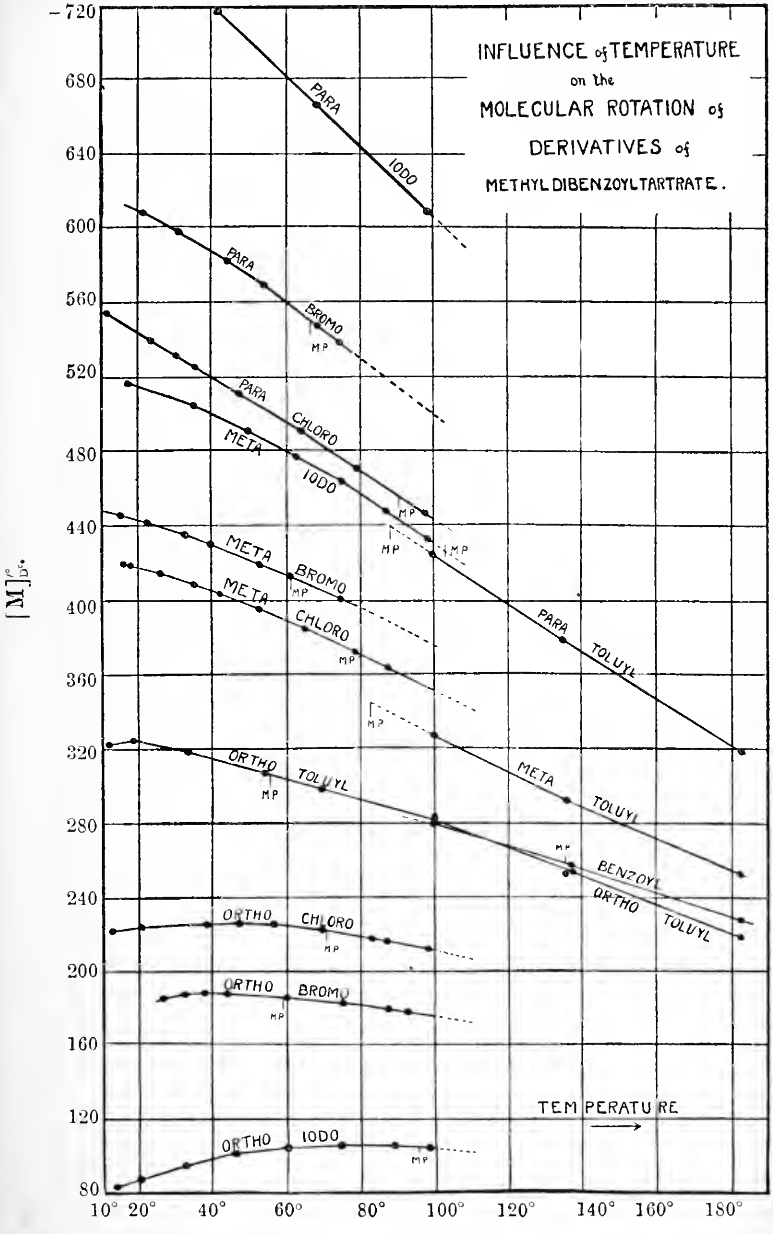
Amyl Esters.

Benzoate.		Toluate.	Bromobenzoate.†	
—	ortho	$[M]_D^{20°}$ $+9{\cdot}37°$ *	$[M]_D^{16°}$ $+5{\cdot}09°$	$[M]_D^{75°}$ $+3{\cdot}87°$
$[M]_D^{22°}$ $9{\cdot}52$ *	meta	$10{\cdot}40$ †	$7{\cdot}32$	$5{\cdot}39$
—	para	$10{\cdot}71$ *	$8{\cdot}62$	$6{\cdot}37$

Amyl alcohol, $[M]_D$ $-3{\cdot}87°$.

* Guye and Chavanne, *Bull. Soc. chim.*, 1896, [iii], **15**, 291.
† Guye and Babel, *Arch. Sci. phys. nat.*, 1899, [iv], **7**, 23.

The rotatory power of this series of compounds is influenced by temperature changes in a remarkable manner, as will be seen by reference to the accompanying diagram. The curve for each compound approximates to a straight line at high temperatures, and in the case of the meta- and para-derivatives, the deviation from a straight line is only slight, until the lowest temperatures are reached. The curves of the ortho-compounds, however, are of a different character; the sensitiveness to heat lessens with a decrease in temperature, and after passing through a region where the rotation is scarcely affected by heat, the temperature-coefficient



actually changes sign, thereby giving rise to a maximum negative value in the rotation. The occurrence of such a maximum was first pointed out by one of us (P. Frankland and Wharton, Trans., 1896, **69**, 1587) in the case of ethyl dibenzoyltartrate and methyl *o*-ditoluoyltartrate.*

Besides the compounds containing an ortho-substituent a maximum value is also exhibited by ethyl dibenzoyltartrate, and in each case the maximum occurs below the melting point. The following table summarises the data with regard to the maximum rotation values, and also the melting points of the compounds in this inquiry.

	Methyl dibenzoyltartrate.	Ethyl dibenzoyltartrate.		Derivatives of methyl dibenzoyltartrate.			
				CH_3.	Cl.	Br.	I.
Melting point...	135·5°	62·5°	*p*-	88·5°	91·0°	66·0°	glassy solid
			m-	83·0	80·0	61·0	103·0°
			o-	56·0	71·0	59·0	95·0
Temperature of maximum rotation value		57·0		19·0	47·5	39·0	82·0
$[M]_D$ (maximum value)		−258·0		−324·5	−226·5	−189·0	−106·5

It will be observed that the melting points of the three methyl dibromobenzoyltartrates, as well as the maximum value of the *o*-bromo-compound, occur at lower temperatures than those of the corresponding chloro-derivatives.

The tendency for the rotatory power to become equalised at high temperatures, as exhibited by the toluoyl compounds, is shared by the remaining members of the series. In other words, the higher the molecular rotation the steeper is the slope of the temperature-rotation curve.

The molecular volumes have been deduced from the experimental data, and compared with the values calculated from Traube's formula †:

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* The instances of a maximum value occurring in the temperature-rotation curve of active substances, have been collected by Patterson and Davidson (this vol., p. 381).

† The values used in calculating the above molecular volumes were: C=9·9; H=3·1; O=5·5 (for either "ester" or "ether" oxygen, which is alone present in these compounds. "Hydroxylic" oxygen has the value 2·3, and this becomes 0·4 when the hydroxyl group is attached to a carbon atom which is also doubly linked to an atom of oxygen as in carboxyl, or when the neighbouring carbon atom is also attached to a hydroxyl group, thus in the ethereal salts of tartaric acid the value of one of the hydroxylic oxygen atoms is 2·3 and that of the other 0·4); "Covolume" = 25·9; double bond = −1·7; 6-atom ring = −8·1; benzene ring = −13·2 (that is, −8·1 + 3 × −1·7) (Traube, *Ber.*, 1895, **28**, 2724, 2924). Cl = 13·2; Br = 17·7; I = 21·4 (Traube, *Ber.*, 1896, **29**, 1024).

We would take this opportunity of rectifying the following values for calculated molecular volumes given in "Some Regularities in the Rotatory Power of Homologous Series of Optically Active Compounds" (Trans., 1899, **75**, 347—371). Thus:

P. 349.........	Methyl benzoylmalate.........	217·8	instead of	215·6
	Methyl *o*-toluoylmalate	233·9	,,	231·7
	Ethyl dibenzoyltartrate	329·5	,,	342·7

	Molecular weight.	Density$^{15^\circ}_{4^\circ}$.	Molecular volume.	
			Found.	Calculated.
Methyl dibenzoyltartrate	386	1·2554	307·5	297·3
,, di-*o*-toluoyltartrate	414	1·2329	335·8	329·5
,, di-*m*-toluoyltartrate		1·2115	341·7	
,, di-*p*-toluoyltartrate		1·2126	341·4	
,, di-*o*-chlorobenzoyltartrate	455	1·3775	330·3	317·5
,, di *m*-chlorobenzoyltartrate		1·3565	335·4	
,, di-*p*-chlorobenzoyltartrate		1·3625	333·9	
,, di-*o*-bromobenzoyltartrate	544	1·6140	337·1	326·5
,, di-*m*-bromobenzoyltartrate		1·6060	338·7	
,, di-*p*-bromobenzoyltartrate		1·5910	341·9	
,, di-*o*-iodobenzoyltartrate	638	1·8095	352·6	333·9
,, di-*m*-iodobenzoyltartrate		1·7900	356·4	
,, di-*p*-iodobenzoyltartrate		[1·7355]	[367·6]	

The bromine and iodine derivatives possess molecular volumes which assume the order para>meta>ortho, but the order of the meta- and para-toluoyl and chlorobenzoyl derivatives is reversed, and in these cases it becomes meta>para>ortho. Instances of a meta-isomeride possessing the largest molecular volume are by no

P. 349	Ethyl di-*p*-toluoyltartrate	361·7	instead of	374·9
	Methyl dibenzoyltartrate	297·3	,,	310·5
	Methyl di-*p*-toluoyltartrate	329·5	,,	342·7
P. 350	Ethyl benzoylmalate	250·0	,,	247·8
	Ethyl *o*-toluoylmalate	266·1	,,	263·9
P. 356	Methyl dibenzoylglycerate	260·3	,,	273·5
	Ethyl dibenzoylglycerate	276·4	,,	289·6
	Propyl dibenzoylglycerate	292·5	,,	305·7
	Amyl dibenzoylglycerate	324·7	,,	337·9

In the dibenzoyl and ditoluoyl compounds, the errors have arisen through inadvertently deducting for only one instead of for two benzene rings in each case :

P. 357	Methyl bromopropionate	115·9	instead of	115·7
	Ethyl bromopropionate	132·0	,,	131·8
	Propyl bromopropionate	148·1	,,	147·9
P. 359	Valeric acid	112·3	,,	114·0
P. 349 & 361	Methyl tartrate	141·0	,,	139·1
	Ethyl tartrate	173·2	,,	171·3
P. 361	Propyl tartrate	205·4	,,	203·5
	*iso*Propyl tartrate	205·4	,,	203·5
	Butyl tartrate	237·6	,,	235·7
P. 354	Methyl glycerate	104·0	,,	102·1
	Ethyl ,,	120·1	,,	118·2
	Propyl ,,	136·2	,,	134·3
	*iso*Propyl ,,	136·2	,,	134·3
	Butyl ,,	152·3	,,	150·4
	*iso*Butyl ,,	152·3	,,	150·4
	Amyl ,,	168·4	,,	166·5
	Heptyl ,,	200·6	,,	198·7
	Octyl ,,	216·7	,,	214·8

In the case of the tartrates and glycerates, the constant error in the series is due to taking the value of both hydroxylic oxygen atoms as 0·4, instead of one as 2·3 and the other as 0·4 (see Traube, *Ber.*, 1895, **28**, 2725, footnote). The argument in the above paper is reinforced by these corrections.

means rare, although its usual value is intermediate between those of the ortho- and para-derivatives.

The compounds described in this paper are very suitable for the study of optical activity. The usual methods employed for the purification of solids are available. The influence of temperature on rotatory power can be studied, since these substances can be maintained in a state of superfusion far below the melting point, and can also be raised to a high temperature without fear of racemisation. The compounds have high rotations, and alteration in a substituent is attended by considerable change in rotatory power.

p-*Chloro-* and m- and p-*iodobenzoic anhydrides* were isolated during the course of the investigation. The preparation of benzoic, *o*- and *p*-toluic and of *p*-bromobenzoic anhydrides is described in the literature.

EXPERIMENTAL.

The chlorides of *p*-chloro- and *p*-iodobenzoic acids, as well as those of the three bromobenzoic acids, were prepared by means of phosphorus pentachloride. Difficulty was at first experienced in obtaining the distilled chloride free from phosphorus, owing to the pentachloride subliming on to cooler parts of the flask, from whence it is only slowly removed by the chloride which distils later. The flask was therefore heated to 140° in an oil-bath at atmospheric pressure, and a current of dry air blown through it by means of a capillary tube until free from pentachloride, after which the distillation under diminished pressure was proceeded with as usual.

For the preparation of the chlorides of the remaining acids—*o*- and *m*-chloro- and *o*- and *m*-iodo-benzoic acids—thionyl chloride was used, and after two distillations in each case a product free from sulphur was obtained. In the use of this somewhat expensive reagent we were able to effect an economy by modifying the usual process described by H. Meyer (*Monatsh.*, 1901, **22**, 415); thus in the preparation of *m*-chlorobenzoyl chloride, 23 grams of acid were divided into three parts, weighing 10, 8, and 5 grams respectively. Ten grams were slowly added to 60 grams of thionyl chloride, and, when the reaction was completed, the excess of thionyl chloride was distilled off under the ordinary pressure (48 grams were recovered), the acid chloride being subsequently distilled under diminished pressure. The recovered thionyl chloride was poured back into the distilling flask, and used for converting the 8 grams of acid, the 5 grams also being ultimately treated in the same way. The combined yields were 21 grams, and on redistillation 19·9 grams. The ordinary method of procedure would require

130 grams, but in the above an excess of six times the weight of thionyl chloride has been maintained with a total outlay of only 60 grams.

*Methyl Di-*o*-chlorobenzoyltartrate.*

A mixture of methyl tartrate and *o*-chlorobenzoyl chloride (22·5 grams) * was gradually heated in a flask to 115°, when hydrogen chloride was evolved. Methyl tartrate (7·2 grams in all) was added from time to time, and the reaction was complete after nine hours' heating, the final temperature being 160°.

The reaction mixture was dissolved in ether (free from alcohol), and shaken with a solution of sodium carbonate until the excess of acid chloride was removed.

The ethereal layer was dehydrated with fused potassium carbonate, and the residue on evaporation set to a crystalline mass on stirring. This (and each similar compound subsequently described) was crystallised from alcohol, after the solution had been boiled with animal charcoal. The yield was 14·4 grams of material melting at 70°. After repeated crystallisation, the melting point was 71°, and the substance had a constant rotation in alcoholic solution. It crystallises in small needles or large prisms, readily soluble in ether or chloroform, moderately so in cold alcohol or benzene, and insoluble in water:

0·2368 gave 0·1488 AgCl. Cl = 15·55.

$C_{20}H_{16}O_8Cl_2$ requires Cl = 15·60 per cent.

Densities determined: *d* 94·5°/4° = 1·3004; *d* 116·0°/4° = 1·2803; *d* 140·0°/4° = 1·2565.

*Rotation of Methyl Di-*o*-chlorobenzoyltartrate.*

Temperature.	α_D (l = 49·92 mm.).	$d^{t°}_{4°}$.	$[\alpha]^{t°}_D$.	$[M]^{t°}_D$.
13·1°	−33·62°	1·3793	−48·83°	−222·2°
20·6	33·71	1·3719	49·22	224·0
39·1	33·50	1·3541	49·56	225·5
46·8	33·47	1·3467	49·79	226·5
56·7	33·11	1·3372	49·60	225·7
69·8	32·36	1·3246	48·94	222·7
83·1	31·40	1·3117	47·95	218·2
87·5	31·01	1·3075	47·51	216·2
99·2	30·28	1·2962	46·80	212·9

Rotation in Ethyl-alcoholic Solution (l = 2 dcm.).

p.	$d^{20°}_{4°}$.	*c*.	$\alpha^{20°}_D$.	$[\alpha]^{20°}_D$.	$[M]^{20°}_D$.
1·606	0·7964	1·279	−1·33°	−51·99°	−236·6°

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* This quantity allows one molecule in excess of that required for the formation of the diacyl compound.

Methyl Di-m-*chlorobenzoyltartrate.*

This was prepared in the same way as the ortho-compound, but a rather higher temperature (140°) was required to induce the evolution of hydrogen chloride, and the reaction continued for thirteen hours. The product separated from alcohol in large, transparent tablets with clearly-defined facets occupying alternate corners, melting at 80°. Its solubility in the ordinary solvents is slightly greater than that of the corresponding ortho-compound:

0·2474 gave 0·1553 AgCl. Cl = 15·53.

$C_{20}H_{16}O_8Cl_2$ requires Cl = 15·60 per cent.

Rotation of Methyl Di-m-*chlorobenzoyltartrate.*

Temperature.	α_D (l = 49·92 mm.).	$d_{4°}^{t°}$.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
16·2°	− 62·32°	1·3556	− 92·09	− 419·0
17·7	62·22	1·3543	92·03	418·7
26·0	61·16	1·3463	91·00	414·1
35·4	59·87	1·3375	89·67	408·0
39·8	59·14	1·3333	88·85	404·3
42·4	58·86	1·3307	88·61	403·2
52·6	57·28	1·3213	86·84	395·1
65·8	55·16	1·3090	84·41	384·1
79·3	52·93	1·2963	81·79	372·2
87·7	51·40	1·2886	79·90	363·6
99·0	49·49	1·2779	77·58	353·0

Densities Determined.

d 66°/4° = 1·3089 d 94·5°/4° = 1·2825
d 116°/4° = 1·2623 d 144·2°/4° = 1·2352

Rotation in Ethyl-alcoholic Solution (l = 2 dcm.).

p.	$d_{4°}^{20°}$.	c.	$\alpha_D^{20°}$.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.
1·961	0·7975	1·564	− 2·71°	− 86·66°	− 394·3

Methyl Di-p-*chlorobenzoyltartrate.*

The usual method of preparation was employed; the reaction between methyl tartrate (7·4 grams) and *p*-chlorobenzoyl chloride (24 grams) commenced at 135°, and was completed in seven hours by gradually raising the temperature to 175°. On freeing the oil from unchanged acid chloride it set to a granular mass on being stirred, and crystallised from alcohol in large prisms or slender needles melting at 91°.

Its solubility is rather greater than that of the preceding isomerides:

0·1885 gave 0·1174 AgCl. Cl = 15·41.

$C_{20}H_{16}O_8Cl_2$ requires Cl = 15·60 per cent.

*Rotation of Methyl Di-*p*-chlorobenzoyltartrate.*

Temperature.	α_D ($l=49·92$ mm.).	$d^{t°}_{4°}$.	$[\alpha]^{t°}_D$.	$[M]^{t°}_D$.
11·8°	−83·33°	1·3660	−122·20°	−556·0
23·9	80·26	1·3536	118·79	540·5
30·4	78·73	1·3470	117·08	532·7
35·9	77·34	1·3414	115·50	525·5
47·2	74·67	1·3298	112·49	511·8
64·1	70·92	1·3127	108·23	492·4
79·5	67·05	1·2967	103·58	471·3
98·0	62·73	1·2784	98·30	447·2

Densities Determined.

d 53·3°/4° = 1·3239 d 67·3°/4° = 1·3195
d 76·2°/4° = 1·3003 d 82·9°/4° = 1·2938
d 86·7°/4° = 1·2929.

Rotation in Ethyl-alcoholic Solution (l=2 dcm.).

p.	$d^{20°}_{4°}$.	*c*.	$\alpha^{20°}_D$.	$[\alpha]^{20°}_D$.	$[M]^{20°}_D$.
1·621	0·7964	1·291	−2·79°	−108·1°	−491·8

p-*Chlorobenzoic Anhydride*.—In the above preparation of methyl di-*p*-chlorobenzoyltartrate about 4 grams of an insoluble substance made its appearance, both in the reaction flask and during the washing with sodium carbonate. It was insoluble in ether or carbon disulphide, and only sparingly soluble in alcohol or benzene. It separated from the latter solvent in long needles—rectangular in section—and after two crystallisations had a constant melting point of 191·5°. Although insoluble in sodium carbonate, it slowly dissolved in aqueous potassium hydroxide, from which *p*-chlorobenzoic acid was obtained on acidifying:

0·2400 gave 0·2314 AgCl. Cl = 23·9.
$C_{14}H_8O_3Cl_2$ requires Cl = 24·1 per cent.

*Methyl Di-*o*-bromobenzoyltartrate.*

The preparation was similar to that of the corresponding *o*-chloro-compound, and, like the latter, it crystallised readily from alcohol. It melts at 59°:

0·1836 gave 0·2950 CO_2 and 0·0515 H_2O. C = 43·82; H = 3·11.
0·1299 „ 0·2098 CO_2 „ 0·0356 H_2O. C = 44·05; H = 3·04.
$C_{20}H_{16}O_8Br_2$ requires C = 44·12; H = 2·94 per cent.

*Rotation of Methyl Di-*o*-bromobenzoyltartrate.*

Temperature.	$\alpha_D^{t°}$ (l=49·92 mm.).	$d^{t°}$.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
27°	−27·42°	1·602	−34·29	−186·5
33	27·54	1·593	34·64	188·4
38	27·52	1·587	34·74	189·0
44	27·31	1·579	34·65	188·5
60	26·64	1·559	34·23	186·2
75	26·02	1·543	33·79	183·8
88	25·26	1·528	33·12	180·2
93	25·02	1·524	32·89	178·9

Each of the above densities was actually determined.

Rotation in Ethyl-alcoholic Solution (l=2 dcm.).

p.	$d_{4°}^{20°}$.	*c*.	$\alpha_D^{20°}$.	$[\alpha]_D^{20°}$	$[M]_D^{20°}$.
1·486	0·8009	1·190	−0·89°	−37·39°	−203°
0·9996	0·7951	0·7948	0·58	36·51	199

Rotation in Pyridine (l=2 dcm.).

p.	$d_{4°}^{20°}$.	*c*.	$\alpha_D^{20°}$.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.
1·408	0·9860	1·388	−0·92°	−33·12	−180°
1·121	0·9831	1·101	0·74	33·61	183

*Methyl Di-*m*-bromobenzoyltartrate.*

Following the methods already described, this compound was first obtained as an oil, which did not crystallise from the ordinary solvents. Crystallisation was, however, ultimately effected by slow evaporation of its solution in a large volume of alcohol. It melts at 61—62°:

0·1064 gave 0·1714 CO_2 and 0·0302 H_2O. C=43·94; H=3·15.
0·1262 ,, 0·2032 CO_2 ,, 0·0354 H_2O. C=43·91; H=3·11.
$C_{20}H_{16}O_8Br_2$ requires C=44·12; H=2·94 per cent.

Densities Determined.

Temperature	32°	40°	45°	53°	61°	70°	80°
Density	1·5823	1·573	1·565	1·556	1·544	1·533	1·520

*Rotation of Methyl Di-*m*-bromobenzoyltartrate.*

Temperature.	α_D (l=49·92 mm.).	$d_{4°}^{t°}$.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
4°	−67·33°	1·620	−83·26°	−452·9°
16	65·73	1·605	82·05	446·3
23	64·75	1·595	81·33	442·4
33	63·30	1·582	80·15	436·0
40	62·18	1·573	79·19	430·7
53	60·00	1·556	77·25	420·2
61	58·70	1·546	76·06	413·7
75	56·40	1·531	73·80	401·4

Rotation in Ethyl-alcoholic Solution (l = 2 dcm.).

p.	$d_{4^\circ}^{20^\circ}$.	c.	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
1·033	0·7777	0·8035	−1·16°	−72·19°	−392·7°
1·3057	0·7941	1·037	1·49	71·85	390·9
1·2592	0·7929	0·9984	1·43	71·38	388·3

*Methyl Di-*p*-bromobenzoyltartrate.*

The crude ester separated from all solvents as an oil, and great difficulty was experienced in crystallising it. The oil which separated from dilute alcohol was removed to a dish and triturated with a pestle. This treatment promoted the growth of a number of centres of crystallisation, and after remaining on porous porcelain for a few days the substance was obtained as a brittle solid. By a repetition of this process it finally yielded well-formed, prismatic crystals from alcohol, melting at 66°:

0·1057 gave 0·0732 AgBr. Br = 29·47.

$C_{20}H_{16}O_8Br_2$ requires Br = 29·41 per cent.

*Rotation of Methyl Di-*p*-bromobenzoyltartrate.*

Temperature.	$\alpha_D^{t^\circ}$ (l = 49·92 mm.).	$d_{4^\circ}^{t^\circ}$.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
21·7°	−88 65°	1·5832	−112·2°	−610·2°
30·7	86·63	1·5724	110·4	600·4
44	83·28	1·5565	107 2	583·1
54	80·85	1·545	104·8	570·3
68 5	76·85	1·5290	100·7	547·7
74·6	75·3	1·5228	99·1	538·9

Densities Determined.

d 70·4°/4° = 1·5273
d 74·6°/4° = 1·5228
d 80·4°/4° = 1·5158
d 89°/4° = 1·5059
d 95·1°/4° = 1·4998

Rotation in Ethyl-alcoholic Solution.

p.	$d_{4^\circ}^{20^\circ}$.	c.	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
1·822	0·7982	1·454	−2 96°	−101·8°	−553·5°
1·766	0·7979	1·409	2·86	101·5	552·1

*Methyl Di-*o*-iodobenzoyltartrate.*

This substance was prepared by heating *o*-iodobenzoyl chloride with methyl tartrate to 120—170° for nine hours. The product obtained after the usual purification separated from alcohol in thin, six-sided plates or leaves, and it was crystallised from this solvent until its rotation in pyridine solution was constant. It melts at 95°. It is only moderately soluble in ether, chloroform, or hot alcohol, and sparingly so in cold alcohol:

0·2149 gave 0·1581 AgI. I = 39·73.
$C_{20}H_{16}O_8I_2$ requires I = 39·81 per cent.

*Rotation of Methyl Di-*o*-iodobenzoyltartrate.*

Temperature.	$\alpha_D^{t^\circ}$ (l = 49·92 mm.).	$d_{4^\circ}^{t^\circ}$.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
14·1°	−11·96°	1·8104	−13·23°	−84·43°
20·0	12·44	1·8037	13·82	88·15
32·1	13·47	1·7900	15·07	96·18
45·7	14·17	1·7746	16·00	102·05
60·0	14·52	1·7584	16·54	105·54
74·7	14·54	1·7420	16·72	106·67
89·1	14·38	1·7257	16·69	106·50
99·0	14·10	1·7145	16·47	105·11

Densities Determined.

d 85·1°/4° = 1·7302
d 94·7°/4° = 1·7194
d 114·7°/4° = 1·6974
d 140·5°/4° = 1·6679

*Methyl Di-*m*-iodobenzoyltartrate.*

This was prepared in the usual manner, and the crude ester was obtained as a viscid syrup, which set to a crystalline mass on cooling. It crystallises from alcohol in slender needles melting at 103°:

0·2355 gave 0·1729 AgI. I = 39·68.
$C_{20}H_{16}O_8I_2$ requires I = 39·81 per cent.

*Rotation of Methyl Di-*m*-iodobenzoyltartrate.*

Temperature.	α_D^{t} (l = 49·92 mm.).	$d_{4}^{t^\circ}$.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
17·8°	−72·14°	1·7866	−80·90°	−516·1°
35·1	69·82	1·7665	79·18	505·1
50·0	67·22	1·7488	77·00	491·3
63·0	64·80	1·7335	74·88	477·8
75·2	62·41	1·7190	72·73	464·0
87·6	59·73	1·7046	70·19	447·8
98·5	57·31	1·6918	67·86	433·0

Densities Determined.

d 67·0°/4° = 1·7288
d 129·6°/4° = 1·6548
d 91·7°/4° = 1·6994
d 143·5°/4° = 1·6382

m-*Iodobenzoic anhydride* separated out during the washing of methyl di-*m*-iodobenzoyltartrate with sodium carbonate. It was crystallised from benzene, a solvent in which it is fairly soluble, and from which it separates in tufts of fine, monoclinic needles, presenting the appearance of thistledown, and melting at 133°:

0·1135 gave 0·1112 AgI. I=52·95.

$C_{14}H_8O_3I_2$ requires I=53·14 per cent.

Methyl Di-p-*iodobenzoyltartrate.*

After the usual process of purification a product was obtained which did not show any signs of crystallisation. The most varied devices for inducing crystallisation proved fruitless, and we had, therefore, to be content with purifying the substance by fractionally precipitating its alcoholic solution with water. The oil obtained after several repetitions of this process was transferred to a large shallow dish containing absolute ether. The warm liquid was kept under diminished pressure until it ceased to lose weight. The ester obtained in this way was a brittle, vitreous solid having a faint green tinge, and this was used for polarimetric examination:

0·1126 gave 0·0814 AgI. I=39·07.

$C_{20}H_{16}O_8I_2$ requires I=39·81 per cent.

Rotation of Methyl Di-p-*iodobenzoyltartrate.*

(Not crystallised, and therefore of doubtful purity.)

Temperature.	$\alpha_D^{t°}$ (l = 49·92 mm.)	$d_4^{t°}$.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
41·5°	−95·70°	1·7060	−112·4°	−717·0°
68·7	87·38	1·6755	104·7	666·5
99·0	78·16	1·6414	95·39	608·6

Densities Determined.

d 67·0°/4° = 1·6780
d 108·5°/4° = 1·6303
d 129°/4° = 1·6082.

p-*Iodobenzoic anhydride* appeared in the course of the above preparation in considerable quantity. Its solubility in organic media is very slight, but it may be crystallised from much chloroform or benzene, and from either solvent is obtained in tufts of short prisms melting at 228°. It dissolves in glacial acetic acid, but in so doing becomes hydrolysed to *p*-iodobenzoic acid:

0·1750 gave 0·1712 AgI. I=52·87.

$C_{14}H_8O_3I_2$ requires I=53·14 per cent.

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CCLX.—*Studies in Chemical Crystallography. Part I. Co-ordination, Isomorphism, and Valency.*

By Thomas Vipond Barker.

The object of this paper is to communicate some unusual * types of isomorphism which have not been recognised previously. It is believed that a critical examination of all such well-established types will lead to the conclusion that in the majority of inorganic compounds the older conception of valency must be altered in some way or other. The comprehensive theory of Barlow and Pope will be criticised, and an attempt will be made to show that it is very difficult, if not altogether impossible, to build up the crystalline structure of many inorganic compounds except on the assumption of a variability of valency volume. It will be shown that the co-ordination theory of Werner brings out pronounced chemical analogies in the great majority of the unusual types of isomorphism, and even serves as a new guide in the recognition of isomorphism, so that it would appear that systematic crystallographic work in the new direction now adumbrated cannot fail to lend precision to what some chemists still regard as a mere classificatory implement.

Historical.

The history of the subjects mentioned in the title may be divided into three periods. The first comprises the discovery of isomorphism by Mitscherlich, and its application by Berzelius to the problems connected with determinations of atomic weights. Mitscherlich recognised that his isomorphous compounds were similar in chemical composition, and Berzelius accepted unreservedly the inference that a knowledge of the molecular composition of one substance determines that of another substance isomorphous with it; and in most cases he deduced the correct atomic weights. The classical examples are selenium and manganese; if potassium sulphate has the molecular formula K_2SO_4, then the composition of the isomorphous potassium selenate is K_2SeO_4, and so on.

During this period there was no structural chemistry in the modern sense of the word, and consequently no theoretical difficulty

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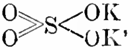
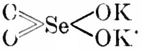
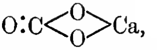
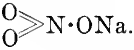
* By "unusual" it is meant that the substance in question exhibits no similarity of chemical constitution when formulated on the conventional lines of valency. Terms like "abnormal" or "anomalous" would be misleading, not only because the number of cases is quite considerable, but also because it seems probable that there is no real difference in principle between the usual and unusual cases. The term "writer" will be employed to designate the compiler (T. V. B.); "author" to any one whose views are criticised.

was involved in accepting a well-known case of isomorphism, namely, that of calcite, $CaCO_3$, and sodium nitrate, $NaNO_3$.

The second period of chemistry is identified with the discovery of the saturation capacity or valency of an element, the conception and development of atom linking, and the formulation of the periodic classification of the elements. These discoveries had a stimulating effect on the study of isomorphism, and served to emphasise the profound connexion which undoubtedly exists between similarity of crystalline form and similarity of chemical structure. The condition underlying the isomorphism of potassium sulphate and selenate was held to be the similarity of valency structure, which is a result of the chemical similarity of the replaceable elements:  $\begin{matrix}O\\O\end{matrix}{>}S{<}\begin{matrix}OK\\OK\end{matrix}$,  $\begin{matrix}O\\O\end{matrix}{>}Se{<}\begin{matrix}OK\\OK\end{matrix}$. Isomorphous replaceability was found to be a periodic function of the elements, for those elements which belong to the same sub-group of the periodic classification as a rule give rise to isomorphous compounds.

The influence of the new theories was not, however, wholly beneficial. It was impossible to formulate calcium carbonate and sodium nitrate in a similar manner, since the doctrine of valency points to the formulæ:  $O{:}C{<}\begin{matrix}O\\O\end{matrix}{>}Ca$,  $\begin{matrix}O\\O\end{matrix}{>}N{\cdot}ONa$. If these formulæ really indicate the internal structures, the observed isomorphism must be due to some obscure, accidental cause. All the experimental facts pointed to a true similarity of crystal structure, but the valency theory involved complete dissimilarity; and the result was that many theorists attempted to narrow down the use of the term isomorphism, and refused to recognise the two compounds as isomorphous.

It is interesting to note that organic chemistry has derived far more benefit from the discoveries of the second period than has inorganic chemistry.

The third period has now commenced. Chemists have begun to question whether the orthodox doctrine of valency is capable of embracing the new types of compounds, especially inorganic, which are rapidly being discovered. The elucidation of the constitution of double salts and of the large class of the cobaltamines and allied compounds is a task which the valency theory in its present form is unable to perform. The most serious attempt to introduce suitable modifications into the older conception of valency is that of Werner, who has advanced the ideas of principal and subsidiary valency and the co-ordination number.

The Method Adopted in Presenting the Crystallographic Results.

As is generally known, the degree of geometrical similarity of two crystalline substances may be measured by the closeness in values of the crystallographic constants; provided that the latter have not been artificially manipulated by multiplying by small rational fractions, the degree of approximation of these constants for two substances may be taken as a true index of similarity of all the measured angles; in other words, it estimates the closeness of the isomorphism. Needless to say, no attempt has been made to produce similarity by such arbitrary treatment in the cases now to be described. It must also be mentioned that in all cases where determinations of the cleavage (cohesion) are recorded they always indicate a close structural resemblance.

It is to be borne in mind that this paper is concerned with the unusual types of isomorphism, that is, those cases devoid of any similarity of valency structure, as, for example, K_2SO_4 and K_2GlF_4. Now there is quite a number of substances which presumably have the same valency structure as, and which are isomorphous with, potassium sulphate, for example, the majority of the sulphates, selenates, chromates, thiomolybdates, and thiotungstates of potassium, rubidium, cæsium, thallium (also of ammonium), and in the same way the number of analogues of potassium glucinum fluoride is not inconsiderable. To give the parameters of all these compounds would only lead to confusion, so they are completely omitted. The existence of such a number of compounds, however, is a convincing proof that the cause of the isomorphism of potassium sulphate and potassium glucinum fluoride underlies the whole series, and the isomorphism of the two compounds cannot be explained away as an accidental property. The number of analogues of each substance mentioned in the following list is given (enclosed in a bracket) immediately after the crystallographic constants of the substance.

Unusual Types of Isomorphism.

The following tables contain the crystallographic constants of a number of unusual isomorphous series of compounds which forms the subject of discussion in succeeding pages. No references are given, since practically all the compounds are fully described in Groth's "Chemische Krystallographie" (which may be regarded as the "Beilstein" of crystallography). The names of those who have recognised the unusual types of isomorphism are given in each case.

Tables of Unusual Types of Isomorphism.

Series I.—Monoclinic System (Marignac).

$CuTiF_6,4H_2O$	$a : b : c$ = 0·7471 : 1 : 0·5564 ;	β = 104°9′	(2).
$CuCbOF_5,4H_2O$	= 0·7627 : 1 : 0·5629 ;	β = 103°20′	(1).
$CuWO_2F_4,4H_2O$	= 0·7648 : 1 : 0·5629 ;	β = 103°14′	(1).

In addition to this series there are two others, namely, the zinc salts of these acids with six molecules of water of crystallisation, and the potassium salts which crystallise with one molecule of water; these additional two series serve to confirm the series just stated in full.

Series II.—Monoclinic System (Marignac).

K_3HSnF_8	$a : b : c$ = 0·6277 : 1 : 0·4928 ;	β = 93°0′	(1).
K_3HCbOF_7	= 0·6279 : 1 : 0·4900 ;	β = 93°14′	(0).

Series III.—Orthorhombic System (Barker).

$K_2SnCl_4,2H_2O$	$a : b : c$ = 0·6852 : 1 : 0·7586	(3).
K_2FeCl_5,H_2O	= 0·6911 : 1 : 0·7178	(4).

Series IV.—Monoclinic System (Barker).

$MnCl_2,4H_2O$	$a : b : c$ = 1·1525 : 1 : 0·6445 ;	β = 99°25′	(1).
$GlNa_2F_4$	= 0·9913 : 1 : 0·6929 ;	β = 99°20′	(0).

Series V.—Tetragonal System (Hiortdahl).

Xenotime, YPO_4	$a : c$ = 1 : 0·6177	(0).
Zircon, $ZrSiO_4$	= 1 : 0·640	(1).
Cassiterite, SnO_2 ($SnSnO_4$)	= 1 : 0·6726	(4).

Series VI.—Tetragonal System (Hiortdahl—Barker).

The isomorphism of the first two was noticed by Hiortdahl.

KIO_4	$a : c$ = 1 : 1·5534	(3).
$CaWO_4$	= 1 : 1·5268	(7).
$KOsO_3N$	= 1 : 1·6319	(1).
$KRuO_4$	= 1 : 1·6340	(0).

Series VII.—Orthorhombic System (? —Barker).

The isomorphism of the first two was mentioned by Marignac in 1867, not as a personal observation, but as a long-recognised fact. The similarity of internal structure was proved by the writer (Trans., 1906, **89**, 1137); the isomorphism of the third member is now pointed out for the first time.

$KClO_4$	$a : b : c$ = 0·7817 : 1 : 1·2792	(8).
$BaSO_4$	= 0·8152 : 1 : 1·3136	(5).
KBF_4	= 0·7898 : 1 : 1·2830	(1).

Series VIII.—Orthorhombic System (Barker).

K_2SO_4	$a:b:c = 0·5727 : 1 : 0·7418$	(15).
K_2GlF_4	$= 0·5708 : 1 : 0·7395$	(4).
$(NMe_4)_2HgCl_4$	$= 0·5766 : 1 : 0·7893$	(1).

*Case VIII*a.—Orthorhombic System (Barker).

$ZnI_2,4NH_3$	$a:b:c = 0·5754 : 1 : 0·7922$	(0).

Series IX.—Monoclinic System (Barker).

$(NH_4)_2SeO_4$	$a:b:c = 1·8900 : 1 : 1·1987$; $\beta = 115°29'$	(2).
Cs_2HgI_4	$= 1·3155 : 1 : 0·9260$; $\beta = 110°4'$	(0).

Series X.—Rhombohedral System (Marx?).

$NaNO_3$	$a:c = 1 : 0·8297$	(0).
$CaCO_3$	$= 1 : 0·854$	(4).

In addition to the above series there are a few others in which the crystallographic approximation is not so good; on this account they need not be considered, especially as they do not offer any new features of theoretical interest. Many analogous cases (generally of a more complicated character) are to be met with in minerals, for example, albite, $NaAlSi_3O_8$, and anorthite, $CaAl_2Si_2O_8$, are closely isomorphous—the difference in composition of these minerals is of the same nature as that exhibited by the first series mentioned in the table.

It may be mentioned that the number of isomorphous substances could be considerably extended in nearly all the series by the preparation of new compounds of analogous valency structure, for the periodic classification enables us to predict within certain limits what compounds should be isomorphous; thus in the case of potassium borofluoride the only analogous compound so far measured is the rubidium salt; it is tolerably certain that when ammonium, cæsium, and thallium salts are prepared and examined, they will prove to be isomorphous.

Previous Explanations of Isomorphism of the Unusual Type.

Isomorphous substances of the usual type have naturally always been accounted for by the similarity of valency structure coupled with the chemical resemblance of the replaceable metals or metalloids; for example, in potassium sulphate and selenate the valency structures are identical, and the replaceable elements, sulphur and selenium, are very closely allied. Here, then, the chemical structures are in complete harmony, and the same is true for, say, two thousand other isomorphous substances. In view of this it is not surprising that attempts have been made to explain the isomorphism of calcite and sodium nitrate in terms of valency; it is true that the structures differ, but, nevertheless, the total sum of the valencies is in each case twelve, and the impossibility of formulating really analogous structures was surmounted by supposing that the sexavalent groups CaC and NaN can replace each other isomorphously; of course, this is begging the question altogether. Moreover, explanations of this nature fail to account for the isomorphous replaceability of the alkali metals by the ammonium radicle; the valency summation for ammonium is nine, whilst for potassium it is only one; the summations in potassium and ammonium chlorides are respectively two and ten, in the sulphates sixteen and thirty-two. One is forced to the conclusion that equality of valency summation has nothing to do with isomorphism.

The other cases of isomorphism of the unusual type, and especially those now recognised for the first time, conclusively prove that isomorphism is a very common property amongst compounds which have no similarity as expressed by the old constitutional formulæ; and it therefore might be hazarded that isomorphism may be totally independent of the chemical structure. It is believed that it will be possible to prove the untenability of this view, and to indicate that it is really valency structure which is at fault. The first step will be to show that the unusual types of isomorphism exhibit periodic regularities.

Periodic Regularities Exhibited by the Unusual Types of Isomorphism.

In series VI and VII of the above tables it is seen that the first two members of each series are chemically very closely related; tungsten and iodine, sulphur and chlorine are members of groups VI and VII of Mendeléeff's periodic classification, the first pair having high, the second pair low, atomic weights. Although not mentioned in the table, it must now be stated that calcium molybdate is isomorphous with calcium tungstate; potassium permanganate with the perchlorate; barium chromate and selenate with the sulphate. It is obvious that, including all members, both usual and unusual, there is a distinct line of division between the upper and lower elements of groups VI and VII of the periodic classification; the elements of lower atomic weight, namely, chlorine, manganese, sulphur, chromium, and selenium, favour the stability of the orthorhombic crystal structure, whilst the elements with higher atomic weight, namely, iodine, molybdenum, and tungsten, favour the stability of the tetragonal structure. Whether the atomic weight of the electropositive part of the molecule is high or low appears to have no decisive effect. Is it a mere coincidence that the atom which more than any other decides stability of crystal structure is that atom which, in the chemical sense, has the unique position, that is, the central atom in the old valency structure, or the co-ordination-nucleus in the new theory?

The regularity noted above is so striking that it may be predicted that when compounds of the type KBF_4, in which boron is replaced by, say, lanthanum, and perhaps fluorine by bromine or iodine, then such compounds will prove to be isomorphous, not with potassium borofluoride, but with potassium periodate and calcium tungstate. It also seems likely that a possible compound, $KFeO_3N$, would belong to the seventh series of the above table.

The two series taken together present all the features of "isopolymorphism." Very often two or more compounds which might reasonably be expected to be isomorphous are found to exhibit pronounced differences in crystalline form, for example, corresponding compounds of chlorine, bromine, and iodine are not always isomorphous, the bromine compound being isomorphous with either the chlorine or iodine compound, the two latter exhibiting no isomorphism. By suitably altering the temperature of crystallisation such a bromine compound may often be obtained in a second form, so that the two forms are respectively isomorphous with the chlorine and iodine compounds; it seems likely that if, say, potassium perbromate could be isolated and measured, it would be found to exist in two forms corresponding with the tetragonal and orthorhombic forms characteristic of the two series under discussion.

The same periodic regularity is traceable in series VIII and IX. Ammonium selenate is isomorphous with the molybdate and also with potassium tungstate; unfortunately, cæsium mercury iodide stands alone, but a comparison of the two series shows that a central atom of high atomic weight favours the stability of the monoclinic structure, whilst central atoms of low atomic weight favour the orthorhombic structure. The large differences in the parameters of ammonium selenate and cæsium mercury iodide are noteworthy, but not unexpected when viewed in the following light. The parameters of potassium sulphate and potassium glucinum fluoride are very close. Now examine the composition of ammonium selenate and the mercury compound; neglecting the electropositive element, it is seen that in one case merely the substitution of the central atom of sulphur by one of selenium has been effected, but in the other case glucinum has been replaced by mercury, that is, the first member of group II by the last member; moreover, the replacement of the four fluorine atoms by four iodine atoms naturally must have a considerable influence on the parameters. The cleavage is the same in the crystals of both substances—a fact which points to true similarity of internal structure.

The Crystal Structure of Isomorphous Substances.

The general similarity of external geometrical form is prima facie evidence of similarity of internal structure, but additional evidence should be forthcoming, as, for example, the determination of the cohesion (cleavage), and perhaps in a less degree the optical properties. Additional proofs of a different kind are derivable from a study of the mutual action of two crystalline substances, the isomorphism of which is suspected. Provided the molecular volumes of the two substances are sufficiently close, it has been found that isomorphous substances are capable of forming homogeneous mixed crystals, of forming parallel overgrowths on each other, and of being mutually active in inducing crystallisation when a supersaturated solution of the one is inoculated with a small crystal fragment of the other.

The experimental verification of close isomorphism in some of the unusual types has been the chief part of the writer's work during the last eight years, and the results have proved satisfactorily the complete character of the isomorphism.

The following may be taken to be the present views concerning the nature of isomorphous structures, and are the result of experimental and theoretical work, some of which even dates back to a time some forty years before the researches of Mitscherlich.

In a given substance each atom and molecule has its appropriate sphere of influence, and when the substance crystallises the molecules take up an homogeneous arrangement. If one or more atoms in the molecule be replaced by one or more atoms of another element, the substances thus derived may prove to be isomorphous. There is only one way of interpreting similarity of all the crystallophysical properties of isomorphous substances; the position of the substituted atom is occupied by the substituent atom; if an atom is isomorphously replaced by a group of atoms, as, for example, potassium by ammonium or tetramethylammonium, then the group takes up the position vacated by the substituted atom. Moreover, the unchanged parts of the structure are but little affected; of course, very slight shifts do occur.

The full meaning of similarity of structure is best illustrated by taking a concrete example. Let it be assumed that the mechanically stable arrangement of the atoms in a crystal of barium sulphate corresponds with the valency structure, that is, that in the crystal the atomic sphere of influence of sulphur is bounded by four atomic spheres of influence of oxygen, two of which perhaps usurp a greater area than those other two, which are partly bounded by an atomic sphere of influence of barium. If this structure is true of barium sulphate, the crystallo-physical properties demand the same arrangement in potassium perchlorate and potassium borofluoride. The conclusions must once more be drawn that in these three substances at least two of the valency structures are wrong, and possibly all three.

The Geometrical and Mechanical Theories of Crystal Structure.

Theories of crystal structure may be divided into two classes, namely, the geometrical and the mechanical. The geometrical theory is concerned with the abstract investigation of the possible kinds of arrangement of matter in the crystal edifice; it is not concerned with the nature of the material particles, which serve as units. The problem confronted by the pure geometrical theory is: what kinds of arrangement of units are possible, which shall be in consonance with the geometrical laws obeyed by crystals? The solution of the problem has been effected, and the results may be regarded as final; the independent investigations of Fedoroff, Schoenflies, and Barlow have led to the unanimous conclusion that there are in all two hundred and thirty possible kinds of arrangement (point-systems).

The mechanical theory begins where the pure geometrical theory ends. It is concerned with the investigation of the mechanical stability of the point-system and the allocation of a particular system to every crystalline substance. It is obvious that the chemical composition now comes into play, and the volumes of the atoms, as also their relative arrangement in the molecule, are other principal factors to be taken into consideration. The complexity of such investigations is probably not even approached by the most abstruse problems in celestial mechanics, and the field as yet is practically unexplored. Perhaps the only work in the mathematical direction is contained in a paper by Lord Kelvin (*Phil. Mag.*, 1902, [vi], **4**, 139). In absence of the necessary mathematical foundation, recent attempts at erecting superstructures must be regarded as tentative. Their usefulness may perhaps be estimated by having regard to the number of initial, arbitrary assumptions on the one hand, and the number of chemical structures thereby correlated on the other. Two different theories have been lately propounded from somewhat different points of view. The theories of Sollas and of Barlow and Pope are alike in that they rest on the assumption that space in crystalline matter is filled up with spherical domains of influence, which, according to Sollas, may be fairly loosely packed, but according to Barlow and Pope are quite closely packed; each atom appropriates a particular domain, but according to Barlow and Pope subsequent compression may squeeze out the interstitial space whereby the atom assumes a polyhedral form. The theories really differ radically in the volume relationships of the various atoms.

The Theory of Sollas.

Sollas takes the volumes of the spherical units to be proportional to the atomic volumes, which are, of course, not the atomic volumes of the elements in the uncombined condition, but in the compounds concerned; nor is the sum of the atomic volumes equal to the molecular volume, since due allowance is made for the interstitial space (*Proc. Roy. Soc.*, 1898, **63**, 270, 286, 296; 1900, **67**, 493; 1902, **69**, 294; 1908, **80**, 267). By ingenious methods he calculates the atomic volumes, and builds up the crystal structure by suitably arranging and packing them together; the structure obtained is in harmony with the observed geometrical form of the crystal, and also with some of its physical properties, for example, cleavage, optics, expansion by heat, and so on.

Perhaps the most convincing work is contained in the first, second, and sixth papers. The first deals with the haloids of the alkali metals crystallising in the cubic system; on account of the inequality of atomic volumes of the halogen and metal, Sollas has to assume that the true structural unit is an aggregate of four molecules. This assumption may or may not be legitimate; at the present time there is no sure method of determining the molecular weights of solids. The second paper presents a very full study of silver iodide, which is polymorphous (hexagonal and cubic); the only point open to criticism appears to be that the structures are quite loosely packed, apart from which the close correspondence of expectation with result in regard to the general physical properties, and in particular the change of density on transformation, is very striking. The most elegant of all, however, is the sixth memoir, in which the three polymorphous forms of titanium dioxide, TiO_2 (or perhaps $TiTiO_4$), as well as cassiterite, SnO_2, receive very full treatment. Sollas's investigations up to the present include examples from the cubic, tetragonal, hexagonal, and orthorhombic systems; it is to be hoped that future work will include some of the simpler unusual types of isomorphism, to which Barlow and Pope's theory in its present form does not appear to be applicable. The strong point in Sollas' theory is that the atomic and molecular volumes receive due recognition. The weak point in some of his work is the loose packing he allows in certain molecular structures, especially in silver iodide. Surely loose packing is equivalent to the assumption that some of the atoms have a greater volume than initially supposed; with sufficiently loose packing it does not seem difficult to obtain any structure whatsoever, irrespective of the "volumes" of the atoms.

The Theory of Barlow and Pope.

These authors have covered much more ground and have attained a great measure of success, especially in organic compounds. The fundamental assumption is that the atomic unit is "approximately" proportional to the valency of the element; atomic and molecular volumes in the ordinary sense are completely ignored. Some matter was introduced into their first paper of an arbitrary character, and calculated to prejudice the theory, namely, the multiplication of parameters by fractional numbers; this by no means affects the greater part of their work, which in the province of organic chemistry would seem to rest on sure foundations. Their conceptions regarding the structure of aliphatic compounds (and perhaps also of aromatic) are in conformity with the stereometric ideas of van't Hoff—the tetrahedral hypothesis. Further, the correctness of the fundamental assumption as to the volume of the carbon atom being four times that of a hydrogen atom, has received most satisfactory confirmation by the recent determinations of the density of hydrocarbons in the liquid condition by Le Bas. The possibility must not be lost sight of, however, that in organic compounds, valency volumes may happen to be proportional to atomic volumes, which may explain the better results obtained in these compounds than those obtained on the inorganic side of chemistry; perhaps it is not unreasonable to infer that the true unit of volume is the atomic, and not the valency volume. The criticisms now offered relate wholly to isomorphous substances. In fairness to Messrs. Barlow and Pope, it must be expressly stated that most of the unusual types of isomorphism on which the present criticism is partly founded have only recently become known.

Barlow and Pope's Method of Treatment with Isomorphous Substances.

It is evident that a sphere of a certain volume representing the atomic influence of a given element can be replaced by a sphere of approximately equal volume without changing the type of structure. In this way the usual types of isomorphism are accounted for; for example, one or more univalent atoms of chlorine can be replaced by a corresponding number of atoms of bromine or iodine; a bivalent sphere representing sulphur by one of the same volume representing selenium, and so on.

A study of the geometrical properties of systems of closely packed spheres of unequal valency volumes has led to the formulation of the following geometrical principles: first, an atom, say, of valency volume two can be replaced by two atoms each of valency volume one without essentially disturbing the degree of close packing or the type of arrangement of the structure as a whole; secondly, if a sphere of valency volume n is replaced by one of volume $n+1$, the whole structure has to be opened out in order to accommodate the larger sphere, and it is found that close packing without "re-marshalling" can only be obtained by the substitution of another sphere of volume m by one of volume $m+1$. Apparently no example has been worked out on the first geometrical principle, but the authors (Trans., 1906, **89**, 1727) indicate that it is applicable to the case of the compounds NH_4IO_3 and $NH_4IO_2F_2$—two univalent atoms of fluorine replacing one bivalent atom of oxygen. A case involving the use of the second geometrical principle has been thoroughly worked out (Trans., 1908, **93**, 1528), namely, sodium nitrate and calcite. In these two compounds the replacement of univalent sodium by bivalent calcium is accompanied by the replacement of tervalent nitrogen by quadrivalent carbon, whereby close packing can be retained without re-marshalling. It is to be noted that nitrogen is held to be tervalent.

Consequences Resulting from the Neglect of Atomic and Molecular Volumes.

The fundamental assumption that the sphere of atomic influence is approximately proportional to the valency and has no immediate connexion with the atomic volume, has both advantages and disadvantages. To take a particular case, say, the haloids of the alkali metals; these are cubic, and Sollas has to assume an aggregation into quadrimolecular groups in order to compensate the inequalities of atomic volume in halogen and alkali. In Barlow and Pope's view, however, the atomic units of halogen and alkali are practically equal *ex hypothesi*, and it is well known that the close packing of equal spheres easily leads to a cubic arrangement. The molecular volumes of potassium chloride and iodide are respectively 37·49 and 53·06, so that we obtain the values 18·74 and 26·53 as the approximate volumes of the potassium atom in these two substances. Now the atomic volume of uncombined potassium is much greater than, and perhaps double, its volume in the combined condition, so that there does not seem to be any reason why the volume should not vary slightly in its compounds.

On turning to the ammonium salts, however, the consequences of the authors' theory hardly appear to be reasonable. Take the case of potassium and ammonium iodides: the molecular volumes are 53·06 and 59·62; the iodine atom in the former has a volume equal to 26·53, but in the ammonium compound the iodine can only have one-eighth the volume of the molecule, since the total valency volume is eight; that is, volume of the iodine equals 7·45. It must be assumed that when potassium is substituted by ammonium the iodine atom experiences a shrinkage equal to about five-sevenths of its volume in the potassium compound. Is it likely that this is really the case? It must be remembered that a comparison is not being made between atomic volumes of an element in the free and combined conditions, but rather its atomic volume in two compounds which have an extraordinarily close chemical relationship.

It may be stated that Barlow and Pope's and Sollas' theories are equally well in harmony with the results obtained by the writer from a study of parallel growths of isomorphous crystals on each other, since here it is the volume of the molecule as a whole, and not of that of any selected atom, which influences the result.

Attempts to Retain a Single Invariable Valency Volume for Each Element.

The authors would assume that the valency volume of an element is constant, no matter whether the element exercises several valency functions or not. In practice they select the lowest valency, and it follows that in their treatment there is no geometrical interpretation of the higher valencies whatsoever. In the metallic sulphides, for example, the bivalency of sulphur has a real, geometrical expression since a two-unit volume is taken to represent the atomic sphere of influence; but the same valency volume would be ascribed by the authors to sulphur in the sulphates, which would seem to be hardly consistent. The chemical properties of barium sulphate unambiguously point to the conclusion that the atom of sulphur plays the principal rôle in the mechanics of the molecule; it is the central atom, and more than any other keeps the molecule together. Now compare barium sulphate with any other simple compound in which the authors admit the presence of an atom of larger valency volume, say, methane. The quadrivalency of carbon, that is to say the power of holding four hydrogen atoms, is interpreted geometrically by the assumption that the carbon sphere has four times the volume of the hydrogen sphere. Would it not be more consistent on general chemical grounds if a similar interpretation were adopted in the case of barium sulphate? that is, that the atom of sulphur has, say, a valency volume of six, whereby its ability to hold four bivalent oxygens would become easier of comprehension.

Even if arguments of the above character are not convincing, some of these authors' published work already shows that the attempt to carry through the principle of unchangeable valency volume leads to damaging results. In the paper on polymorphism already cited (Trans., 1908, **93**, 1553) the valency volume of manganese is discussed. From the analogy between manganese carbonate and calcite the valency volume is deduced to be two; but in mentioning the undoubted isomorphism of potassium perchlorate and permanganate with barium sulphate they fall into difficulties. Their previous work on halogen compounds had shown that chlorine has the valency volume one, and in attempting to carry through the principle of invariability of valency volume there is no other alternative but to assume that in the perchlorate the valency volume of chlorine is again one. The isomorphism of potassium perchlorate and barium sulphate now presents no difficulty; the replacement of potassium by barium opens up the structure, so that chlorine can be replaced by the bivalent sulphur. The isomorphous replaceability of chlorine by manganese shows, however, that manganese has a unit valency volume. How do the authors reconcile this with the previous result? Instead of admitting variability of valency volume (which, by the way, is reasonable on chemical grounds), Barlow and Pope conclude that the valency volume has some constant value, lying somewhere between one and two. If this is true, it reflects discredit on calcite, sodium nitrate, manganese carbonate, potassium permanganate and perchlorate, and barium sulphate, for all these compounds are intimately connected by the chain of reasoning.

Formal Proof of Variability of Valency Volume, and Conclusions Regarding Barlow and Pope's Theory.

The writer's recognition that many salts of the halogen- are isomorphous with those of the oxygen-acids (compare series VII—IX) superimposes difficulties of a higher order, and if it is granted that the conception of valency volume is really correct, it apparently furnishes a rigid proof that valency volume is variable. Let us apply the second geometrical principle to the study of a concrete example, say, potassium perchlorate and potassium borofluoride. Following Barlow and Pope, the volume of the former compound is taken as ten; whilst the element boron has presumably the valency volume three. Therefore, in replacing the univalent chlorine by the tervalent boron, the operation leads to an increment of two volume units, and in order to restore close packing without re-marshalling, two other volume units must be added somewhere else. The total increment, then, is four units of valency volume;

adding this to the previous ten, we obtain fourteen as the valency volume of the borofluoride. Now of these, only four are taken up by the potassium and boron, which leaves ten units to be divided amongst the four fluorine atoms; fluorine, then, can certainly not have a unit valency volume in the borofluoride, although all the halogens are supposed without exception to have a unit valency volume. Barlow and Pope's point of view in regard to compounds of the second order is really tantamount to regarding them as molecular compounds; for example, if the valency volume of nitrogen is always three, their geometrical interpretation really amounts to the formula NH_3,HCl for ammonium chloride. If potassium borofluoride is supposed to have the analogous formula BF_3,KF, it is now possible to see how the ten units of valency volume can be rationally distributed; three each to the first three fluorines and the tenth to the unique fluorine. This would, however, involve a variation of valency volume in one and the same substance. If, again, the valency volume of boron is taken to be five, the whole increment in passing from perchlorate to borofluoride will be eight units, which added to ten make eighteen; subtracting six units for the group KB, twelve is obtained—three for each fluorine atom. This procedure would correspond with a constitution for the borofluoride in which the potassium is directly bound to boron, and pairs of fluorine atoms are further linked together by double bonds. Needless to add, the writer does not necessarily insist on any particular value for fluorine. The values obtained being only true provided the chlorine in potassium perchlorate has a unit valency volume.

It is suggested to Messrs. Barlow and Pope that great difficulties stand in the way of a general application of their valency volume theory to inorganic compounds.

Before closing this section the writer would call the attention of chemists to a conclusion concerning the structure of polymorphous modifications, which follows immediately from Barlow and Pope's method of treatment, namely, that polymorphous modifications of a substance are geometrical isomerides, the separate stability of which is wholly bound up with the crystalline condition. This conclusion seems to be legitimate, and is in harmony with the crystallochemical properties of such substances. During the process of crystallisation it seems feasible to suppose that slight shifts take place amongst the atoms so as to ensure close packing and interlocking of the molecules. On lowering the temperature of the crystal beyond the transition point, the arrangement becomes mechanically unstable, and further shifts take place among the atoms. The configuration of any selected molecule would be different in the two modifications, the difference being comparable perhaps with the difference between the configurations of *syn*- and *anti*-substances in the liquid state. On melting either modification the cause for the slight shifts (that is, the necessity of close packing) disappears, and one type of molecule results. It is urgently desirable that the term polymorphism should be always retained for "isomerides," which have no separate existence in the liquid state; the evidence for the so-called chromoisomerism is exceedingly scanty, and no crystallographic determinations appear to have been made. It does not seem warrantable to designate polymorphous modifications as isomerides until a difference in chemical properties shall have been established by reactions carried out in the solid condition; and even when this has become possible, a strict adherence to the term polymorphism would be calculated to prevent misinterpretations.

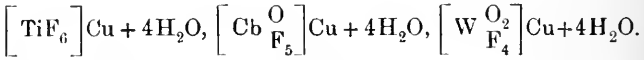
Application of Werner's Co-ordination Theory to the Unusual Types of Isomorphism.

Werner's theory undoubtedly marks a great advance in chemical theory, which seems likely to lead to a development in inorganic chemistry as important as that brought about by the hypothesis of atom linking and of the tetrahedral grouping round carbon in the domain of organic chemistry. It is obvious that our knowledge concerning the true signification of co-ordination is still in the pioneering stage. The doctrines of principle and subsidiary valencies involve some contradictions; thus, applying Werner's definitions to the study of the ammonium salts, it will be found that nitrogen is either quinquevalent or univalent accordingly as the formula is interpreted. Again, with respect to the co-ordination value of bi- or ter-valent atoms, he has not sufficiently made clear that the occupation of only one co-ordination position by such an atom is only possible when the principal valency of the central atom is proportionally increased.

It has already been pointed out that the old theory of valency structure fails to give any useful information concerning the chemical structure of isomorphous substances of the unusual types; also, that the valency structure of these compounds does not correspond with the structure of the molecule in the crystalline state. It will now be shown that the co-ordination theory is, at any rate, capable of bringing out most startling chemical analogies, which fact makes it probable that the theory expresses some condition or other in the inorganic molecule, which, however indefinite it may appear in the present state of knowledge, is likely to attain geometrical precision by the application of crystallographic methods.

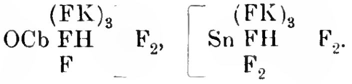
A large number of compounds described in this paper, or, at any rate, compounds of analogous types, have been already formulated by Werner as co-ordination compounds. In the following formulæ Werner's mode of representing the co-ordination structure is adopted.

Series I.



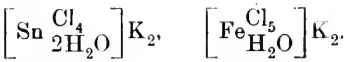
$$\left[TiF_6\right]Cu + 4H_2O,\ \left[Cb\begin{matrix}O\\F_5\end{matrix}\right]Cu + 4H_2O,\ \left[W\begin{matrix}O_2\\F_4\end{matrix}\right]Cu+4H_2O.$$

Series II.



$$\left[OCb\begin{matrix}(FK)_3\\FH\\F\end{matrix}\right]F_2,\ \left[Sn\begin{matrix}(FK)_3\\FH\\F_2\end{matrix}\right]F_2.$$

Series III.



$$\left[Sn\begin{matrix}Cl_4\\2H_2O\end{matrix}\right]K_2,\ \left[Fe\begin{matrix}Cl_5\\H_2O\end{matrix}\right]K_2.$$

Series IV. $[Mn\ 4H_2O]K_2$, $[GlF_4]Na_2$.

In the remaining series, with the exception of the tenth, the co-ordination number of the central atom is evidently four. Only the following compounds have been expressed as co-ordination compounds by Werner: $[OsO_3N]K$, $[BF_4]K$, and GlF_4K_2, but these are representatives of the sixth, seventh, and eighth series; it will not be disputed that the remaining isomorphous compounds have also the co-ordination constitution. From analogy it may be assumed that the fifth, ninth, and tenth series present the same features of chemical constitution, although this involves a co-ordination number three for carbon and nitrogen in these particular cases.

Case VIII*a* deserves special mention. The isomorphism of this compound with potassium glucinum fluoride leads to the assumption that the internal structures are similar in the following sense: $[Zn(NH_3)_4]I_2$ and $[GlF_4]K_2$; and a special item of interest becomes apparent: the positive ion of one compound is analogous to the negative ion of the other. The ammoniacal compound is very stable in solution, and is stated to crystallise very well; the electrical character of the solution has, however, not been investigated. Since the substance is not supported by others, no further inferences are justifiable at present.

Co-ordination evidently supplies a medium in which analogy of chemical composition in isomorphous compounds of the kinds now under discussion comes strongly into the foreground; this is more than can be said of any other system of formulation. There is no analogy, for example, in the third series when the compounds are formulated on the molecular type, $2KCl,SnCl_2,2H_2O$ and

$$2KCl,FeCl_3,H_2O,$$

or on the complex salt type, $K_2SnCl_4,2H_2O$ and K_2FeCl_5,H_2O; with the co-ordination formulæ, on the other hand, a close correspondence of chemical type becomes immediately obvious, and it may be added that it was Werner's formulation that suggested to the writer the advisability of finding out whether these compounds are isomorphous. The fourth series is in some respects the most remarkable of all, for not only is the positive ion of one in correspondence with the negative ion of the other, but also each co-ordinated water molecule is replaced by a co-ordinated atom of fluorine.

The Nature of Co-ordination.

Co-ordination in Werner's estimation, when put into a tangible form, appears to be principally of a geometrical character; the parts co-ordinated with the central atom by subsidiary valencies are in the first shell of attraction, whilst the unco-ordinated parts (generally separately ionisable) are in a second, outer shell. This idea must not, however, be taken too literally, for it does not appear necessary that the unco-ordinated parts should be very far away from the central atom. It must be remembered that a sphere of given volume can be surrounded by twelve spheres of the same volume, so that each of the twelve is touching the central sphere. The maximum co-ordination number appears to be six (in rare cases up to eight), so that it is quite possible for the unco-ordinated atoms (or a part of the unco-ordinated groups) to be in contact with the central atom. Perhaps the process of co-ordination implies a transference of all the electric charges to the central atom, the unco-ordinated parts retaining their charges, so that in the undissociated condition there is positive or negative charge of a certain value on the central atom, and charges of equal and opposite character on the parts unco-ordinated. In this way a subsidiary valency implies a union, in which the parts give up their charges to the central atom; a principal valency, on the other hand, implies that the charge is retained. Whenever dissociation takes place, it is natural to suppose that the primary result is the ion of that co-ordinated complex, which in the undissociated condition already has an electrical charge. The limitation to the co-ordination number is possibly due to steric hindrances.

The results which have been discussed in this paper will perhaps help to strengthen belief in the co-ordination theory, and may contribute to the advancement of crystallography in the estimation of chemists. The main chemical results have already been summarised in the argument. Other conclusions, mostly of a crystallographic character, are:

(1) A greater number than was previously supposed of iso-

morphous inorganic substances have probably a co-ordinative constitution.

(2) The stability of the crystal structure adopted by certain series of isomorphous substances of the unusual type seems to depend chiefly on the values of the atomic weights of the central atom.

(3) From Barlow and Pope's interpretation of crystal structure it is inferred that polymorphism is a species of geometrical isomerism.

(4) Co-ordination must be taken into account in any theory which endeavours to correlate chemical composition and crystalline form.

(5) Many new unusual types of isomorphism are described, and it is concluded that those molecules of water of crystallisation which are really co-ordinated can be replaced isomorphously by halogen atoms.

(6) It is probable that a future application of the co-ordination theory would effect great simplification in regard to those minerals the composition of which appears to be very complicated.

The writer hopes to extend the subject of this paper on the experimental side.

In conclusion, the writer wishes to express his grateful thanks to Professor H. L. Bowman and also to Sir Henry A. Miers for valuable suggestions which they have offered. The development of the paper has been greatly influenced by frequent discussions on chemical subjects with Mr. J. E. Marsh, and the writer has great pleasure in acknowledging the value of his criticisms.

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CCLXI.—*The Constitution and Reactions of Thiocarbamides.*

By Augustus Edward Dixon and John Taylor.

Those who have studied the chemistry of "thiocarbamide" and of its monohydric substitution derivatives are aware how difficult it is to decide the constitution of many of these substances.

Tetrasubstituted derivatives are generally regarded as built on the type of thiocarbamide, $NH_2\cdot CS\cdot NH_2$, but, outside this one class, a good deal of uncertainty exists concerning the molecular structure.

"Thiocarbamide" itself, when reacting with other compounds, so frequently yields compounds containing the nucleus of iminothiocarbamic acid, $NH_2\cdot C(:NH)\cdot SH$, that most chemists now seem disposed to regard it as having the constitution just formulated, and to designate it "thiourea." This, of course, amounts to selecting, for the static configuration of the molecule, the reaction-formula which best consists with its general chemical activities.

More difficulty is encountered in the case of mono-, di-, and trisubstituted "thiocarbamides"; for whilst, in some reactions, these yield derivatives of iminothiocarbamic acid, yet in many others the products contain instead the nucleus of thiocarbamide. By no one reaction-formula is it possible to sum up the general chemical activities of such compounds; and hence, as a rule, it is sought to explain the facts by the assumption that, previously to interaction, or at the moment of interaction, a tautomeric change may occur. How this change is supposed to come about, depends obviously on what view is held as to the constitution of the original "thiocarbamide"; but essentially the idea is, that a thiocarbamide may become a thiourea, or vice versa, according to the conditions:

$$\begin{matrix}NH_2\\NH_2\end{matrix}\!>C{:}S \longleftrightarrow \begin{matrix}NH_2\\NH\end{matrix}\!\geqslant C{\cdot}SH.$$

Usually, the change is supposed to be from thiocarbamide to thiourea, but sometimes the reverse order seems to be implied.

Whatever view may be held as to the static configuration of these substances, to command general acceptance it must be consistent with two facts of experience. The first of these is, that however any given "thiocarbamide" may be constituted, the static constitution is perfectly definite, no second form being known to exist*; for example, if phenylthiocarbamide has the configuration represented by the formula $PhNH\cdot CS\cdot NH_2$, neither of the desmotropes, $PhNH\cdot C(:NH)\cdot SH$ and $PhN:C(NH_2)\cdot SH$, has yet been obtained.

The second fact is, that the various classes of "thiocarbamides" exhibit from one to another no sudden or abrupt variations, either as regards methods of formation, general properties, or chemical activities. On the contrary, their resemblances are of the closest kind; indeed, save for the variability of constitution displayed by certain of their products of interaction, it would be difficult to specify any essential difference between the classes beyond what can be accounted for by their respective degrees of substitution.

If certain of these compounds are thiocarbamides and others thioureas, some sort of explanation is needed to account for their general homogeneity in the respects mentioned above. It has, in

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* Under the term "thiocarbamide," forms such as $NH_2\cdot C(:NH)\cdot SMe$ are not here included, these being designated "ψ-thioureas."

fact, already been suggested that, for the transformation of a thiocarbamide into a thiourea, nothing more is required than the transfer of a single hydrogen atom from its original attachment at nitrogen to a new one at sulphur; that such a shifting might easily occur; and that there is little reason to suppose that it would modify to any great extent the properties of the resultant desmotropic form.

That it might occur, and perhaps readily, is indisputable; but, that a thiourea would be likely to manifest substantially the same properties as a thiocarbamide is a proposition not yet supported by any evidence, and (as will presently be shown) apparently in conflict with certain facts.

In the following pages we shall endeavour to supply answers to the following questions:

(1) Have any of the so-called "thiocarbamides" the static configuration of iminothiocarbamic acid?

(2) If not, do thiocarbamides, when yielding derivatives of the latter, undergo preliminary tautomeric change?: and if such change does not occur, by what mechanism is a thiourea form produced?

Evidence bearing on these issues will be adduced (*a*) from a consideration of the principal synthetic methods by which "thiocarbamides" are obtained; (*b*) from a comparative study of their properties and those of some allied compounds of known constitution; (*c*) from certain facts which have been secured in the course of a research, the details of which are given below.

Evidence from Synthetic Methods. I.—*Tetrasubstituted Derivatives.*

This class, since it presents no difficulty, may be disposed of forthwith. Tetraphenylguanidine, $NH{:}C(NPh_2)_2$, on treatment with carbon disulphide, exchanges $NH{:}$ for $S{:}$, thereby yielding $CS(NPh_2)_2$; the latter compound, when hydrolysed, furnishes neither aniline nor phenyl mercaptan, but diphenylamine instead (Bernthsen and Friese, *Ber.*, 1882, **15**, 1531). Moreover, the same tetraphenylthiocarbamide results from the warming together of thiocarbonyl chloride and diphenylamine (Bergreen, *Ber.*, 1888, **21**, 340), a method of special importance, as showing that a thiocarbamide can be formed by the withdrawal, from an amine, of a single hydrogen atom, which latter does not become joined to the sulphur of the thiocarbamic constituent, but is eliminated from the system in the form of hydrogen chloride. There can be no reasonable doubt that the above compound is a thiocarbamide; but in any case, the issue is settled by the fact that a trisubstituted "thiocarbamide," with an alkyl haloid, yields an isomeric substance, $R_2N\cdot C(:NR)\cdot SAlk$, different in properties from that resulting from the interaction of a disubstituted thiocarbamyl chloride and a secondary amine.

II.—*Symmetrical Disubstitution Derivatives.*

Here, at first sight, the problem as to constitution appears to be of the simplest kind. A thiocarbimide, $X\cdot NCS$, yields with a primary amine, $Y\cdot NH_2$, a compound indistinguishable from that produced from $Y\cdot NCS$ and $X\cdot NH_2$. The natural interpretation of these facts is, that a single hydrogen atom, passing from the amine, is transferred to the nitrogen atom of the thiocarbimide:

$$X\cdot NCS + Y\cdot NH_2 = XNH\cdot CS\cdot NHY;$$
$$Y\cdot NCS + X\cdot NH_2 = YNH\cdot CS\cdot NHX.$$

For, in no other way can the constituents directly produce the same compound; thus, for example, if the hydrogen atom, supplied by the amine, joined itself to the sulphur atom of the thiocarbimide, two different substances must be formed:

$$X\cdot NCS + Y\cdot NH_2 = XN:C(NHY)\cdot SH;$$
$$Y\cdot NCS + X\cdot NH_2 = YN:C(NHX)\cdot SH.$$

If two hydrogen atoms are transferred from the amine, one must go to the sulphur and one to the nitrogen; and the results would be the same as those last formulated. Besides, there is no ground for supposing that two hydrogen atoms are concerned in these changes; for a thiocarbimide can equally well unite with a secondary amine, which, of course, does not contain two available hydrogen atoms—yet the product is a "thiocarbamide," as before.

Some other synthetic methods demand consideration: (i) Thiocarbanilide is produced, together with thiocyanic acid, by the replacement of the NH-group of diphenylguanidine by S: (Hofmann, *Ber.*, 1869, **2**, 406):

$$CS_2 + NH:C(NHPh)_2 = H\cdot SCN + SC(NHPh)_2.$$

(ii) Carbodiphenylimide unites with hydrogen sulphide at the ordinary temperature, yielding thiocarbanilide (Weith, *Ber.*, 1874, **7**, 1303):

$$C(NPh)_2 + H_2S = CS(NHPh)_2.$$

In the latter synthesis (ii), it is conceivable that the compound $PhNH\cdot C(:NPh)\cdot SH$ might be produced, but the former (i) flatly contradicts this view. So far therefore as thiocarbanilide is concerned, it is quite clear that if it possesses, when in the static condition, the configuration last formulated, that configuration must be acquired through the occurrence of intramolecular change.

What applies to thiocarbanilide will hold good, presumably, for other *ab*-disubstituted "thiocarbamides," since these are produced by synthetic methods of a like kind; for example, if diphenylthiocarbamide cannot exist as such, but changes spontaneously into diphenylthiourea, one must suppose equally that phenylethylthiocarbamide, methylethylthiocarbamide, and so on, are really thioureas, in which case their constitutions must be $PhN\colon C(NHEt)\cdot SH$, $MeN\colon C(NHEt)\cdot SH$, etc., or else, $PhNH\cdot C(\colon NEt)$,

$$MeNH\cdot C(\colon NEt)\cdot SH,$$

etc., unless it is assumed that they are mixtures. From the purely synthetic aspect, there is not the slightest reason for holding such views.

III.—*Trisubstitution Derivatives.*

The two principal methods for preparing hydrocarbon derivatives of this class are: (i) union of a thiocarbimide with a secondary amine:

$$R\cdot NCS + R_2NH = CSN_2HR_3;$$

(ii) interaction between a primary amine and a disubstituted thiocarbamyl chloride:

$$R_2N\cdot CSCl + R\cdot NH_2 = HCl + CSN_2HR_3.$$

Neither of these methods leads, of itself, to a definite conclusion as to the structure of the product. If, however, analogy may serve as any guide, it may fairly be supposed that the hydrogen atom of a secondary amine plays the same part as that in a primary amine; that is, in method (i) it passes to the nitrogen of the thiocarbimide, thus producing a thiocarbamide, $RNH\cdot CS\cdot NR_2$. Again, since a secondary amine yields up its single hydrogen atom to the chlorine of a thiocarbamyl chloride, thereby producing an undoubted thiocarbamide, there is no particular reason for supposing that, in the corresponding reaction where a primary amine is employed, the hydrogen atom should have a different function; and if, as before, it simply displaces the chlorine atom, the residues, $R_2N\cdot CS\cdot$ and $\cdot NHR$, will unite to form a thiocarbamide. Of course, a transformation of the product might possibly come about, but the synthetic methods give no suggestion of this; the most that can fairly be said is, that it is not impossible for a thiourea form to originate, either directly or indirectly, through the two processes named.

IV.—*Other "Thiocarbamides."*

The remaining classes may conveniently be considered together, since all are producible by a single reaction, namely, the transformation of the corresponding ammonium thiocyanates. Various other methods of preparation are available, but as this one is common, and the properties of the resultant compounds are much alike, it may be taken as highly probable that the transformation (whatever its nature) runs always the same course.

Ammonium thiocyanate yields "thiocarbamide"; similarly, a monosubstituted ammonium thiocyanate yields a monosubstituted "thiocarbamide," and a disubstituted ammonium thiocyanate, an unsymmetrical (or *aa*-) disubstituted "thiocarbamide." This change, assuming it to be uniform, and the nitrogen atoms of the product to be tervalent, is plainly attributable to the movement of a single hydrogen atom from the combined amine, for a tri- or a tetra-substituted ammonium thiocyanate fails to undergo the transformation.

Heat is necessary for the latter, a condition tending strongly to determine thiocarbimidic function in the case of compounds, R(CNS), which can act both as thiocarbimide and as thiocyanate; in such compounds, R is a well-marked acyl radicle (see, for example, Dixon and Hawthorne, Trans., 1906, **89**, 468). Certain alkyl thiocyanates, also, when heated, tend to acquire, although much less readily, the thiocarbimidic form, and hence, since hydrogen stands more or less intermediate between acyl and alkyl radicles, it might well be anticipated that thiocyanic acid, at high temperatures, would have the power to behave as H·NCS, or thiocarbimide. An ammonium thiocyanate therefore, when heated to incipient dissociation, would presumably consist of a mixture of free base, thiocarbimide, thiocyanic acid, and salt; and if, at this temperature, the combination product of the first with the second (that is, the corresponding "thiocarbamide") were sufficiently stable, a certain quantity of it must be formed and continue to exist, the amount, of course, depending on various circumstances.

According to this view, the transformation of an ammonium thiocyanate into a thiocarbamide is but a special case of the union between a thiocarbimide and an amine; the conditions of reaction, however, are not quite the same, and may be unfavourable to the production of a high yield, since the reaction product is itself dissociable by heat.

Although, as just stated, the thiocyanate transformation leads probably to the formation of substances having a uniform constitution, most likely thiocarbamidic, the possibility of a thiourea form is not excluded. By the union of a thiocarbimide with ammonia, the same "thiocarbamide" is produced as that from the molecular rearrangement of a primary ammonium thiocyanate, and hence, unless it be assumed that ammonia, with a thiocarbimide, behaves differently from a primary amine, there is some further support for the view that the product is a true thiocarbamide. Nevertheless, such evidence is by no means conclusive, and must not be overrated.

"Thiocarbamide" itself is obtainable by the reduction of *iso*-perthiocyanic acid, a substance reputed to contain the atomic complex, ·NH·CS·NH· ; this fact, however, furnishes no trustworthy guide as to structure, for the molecule, subsequently to its production, might possibly undergo desmotropic change.

Evidence from Properties.

As the refraction value of singly-linked sulphur is perceptibly different from that of doubly-linked sulphur, the idea suggested itself of attempting to decide between the thiourea and the thiocarbamide configurations by molecular refractometric measurements. Such measurements, however, by reason of certain perturbing factors not yet very well understood, are sometimes difficult of application, save by reference to compounds the constitution of which is already known—a method, in this case, obviously inapplicable.

Allylthiocarbamide was selected for experiment, on the principle that whether one of the nitrogen atoms is singly- or doubly-linked is not likely to have much effect on the molecular refraction, whereas, for the *D*-line and on the $n-1$ formula, the value, if doubly-linked sulphur be present, would probably come about two units higher than if the sulphur were singly-linked. Two fairly concordant determinations, made in alcoholic solution, gave M_D 62·4 and 62·6 respectively. It has been shown by Hawthorne (Trans., 1906, **89**, 564) that the mean molecular refraction of the whole group, ·N⁚C⁚S, is about 27·8, whilst that of the allyl radicle, as calculated from Brühl's measurements of allyl chloride (*Annalen*, 1880, **200**, 139), is about 24. Hence the calculated M_D for allylthiocarbimide is about 51·8, a number agreeing fairly with that obtained experimentally by Hawthorne (*loc. cit.*), namely, 51·65. For NH_3, M_D = about 8·7, so that the combination product might be expected to have $M_D = 51·65 + 8·7 = 60·35$, minus, of course, whatever refraction value may be lost through the opening up of double linkings previously existing in the thiocarbimidic group. So far from any diminution being observed, however, it is quite the other way about, the mean molecular refraction for allyl "thiocarbamide," namely, 62·5, exceeding by 2·15 units the sum-total of the molecular refractions of the constituents. Whatever the cause of such enhancement may be, it seems doubtful, in the present state of our knowledge, whether this particular physical method can afford help towards the solution of the problem at issue.

Incidentally, too, it is worth noting that although phenylthiocarbimide and allylamine yield the same product as allylthiocarbimide and aniline, the sum-totals of the molecular refractions of the respective constituents are not the same. For the *D*-line, and on the $n-1$ formula, the following determinations of molecular refraction appear to be trustworthy:

$$\begin{array}{lr} \text{Ph·NCS} = & 77{\cdot}6 \\ C_3H_5\text{·}NH_2 = & 31{\cdot}4 \\ \hline & 109{\cdot}0 \end{array} \qquad \begin{array}{lr} C_3H_5\text{·NCS} = & 51{\cdot}65 \\ \text{Ph·}NH_2 = & 53\ 36 \\ \hline & 105{\cdot}01 \end{array}$$

A determination made by us of the molecular refraction of phenylallylthiocarbamide (in alcoholic solution) gave the number 105·8; for the present we do not know what significance to attach to it.

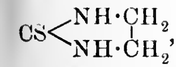
The class of evidence next to be considered has hitherto received less attention than it appears to deserve. Carbamic acid, $O{:}C(NH_2){\cdot}OH$, and thiocarbamic acid, $O{:}C(NH_2){\cdot}SH$, do not seem to be capable of existence, at least, in ordinary circumstances; and hence there is no reason to anticipate that their imino-derivatives—that is, $NH{:}C(NH_2){\cdot}OH$ and $NH{:}C(NH_2){\cdot}SH$ respectively—if able to exist at all, would be anything like stable. The former, iminocarbamic acid, is unknown.

Again, the substitution of the imino-group for an oxygen atom, joined to a carbon atom which already holds the amino-group, tends strongly to enhance the basicity of the resultant new molecule; thus, iminocarbamide, $NH{:}C(NH_2)_2$ (guanidine), is a powerful caustic base, very different from urea, $O{:}C(NH_2)_2$; $O{:}C(NH_2){\cdot}SEt$ (xanthogenamide) is a somewhat indifferent substance, whereas $NH{:}C(NH_2){\cdot}SEt$ (ethyl-ψ-thiourea) is a well-marked base; and the like holds if $MeCO{\cdot}NH_2$ (acetamide) is compared with

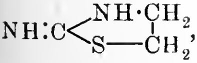
$$MeC({:}NH){\cdot}NH_2$$

(acetamidine). Moreover, $NH{:}C(NH_2){\cdot}OMe$ (methyl-ψ-urea) and $NH{:}C(NH_2){\cdot}SMe$ resemble one another in being very distinctly basic—they are both decidedly unstable.*

Between two dihydric (ethylene) derivatives, this kind of distinction is especially clearly cut; for ethylenethiocarbamide,



$CS{<}\begin{matrix} NH{\cdot}CH_2 \\ NH{\cdot}CH_2 \end{matrix}$, fails to unite with acids, whilst the isomeride,



$NH{:}C{<}\begin{matrix} NH{\cdot}CH_2 \\ S{-\!\!-}CH_2 \end{matrix}$, or ethylenethiourea, is a strong base—in short, the combination $NH{:}C(NH_2){\cdot}$, in simple molecules appears to carry with it a definitely alkaline character.

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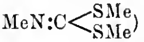
* Delépine points out (*Bull. Soc. chim.*, 1910, [iv], **7**, 991) that thiosulphocarbamic esters (for example,

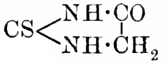
$S{:}C{<}\begin{matrix} NMe_2 \\ SMe \end{matrix}$) are non-basic, whereas the iminocarbonic isomerides (for example,



$MeN{:}C{<}\begin{matrix} SMe \\ SMe \end{matrix}$) are basic.

In view of these facts, it is more than doubtful if "thiocarbamide" is $NH{:}C(NH_2)\cdot SH$; for, if analogy may here serve as guide, iminothiocarbamic acid would probably be very unstable, or perhaps incapable of existence. If able to exist, it should be a strongly marked base, alkaline to litmus, and might be expected to decompose, with formation, not of ammonium thiocyanate, but of hydrogen sulphide and cyanamide.

The amides proper, on the other hand, show in general no especially pronounced basic character. Urea, in fact, is surprisingly feebly basic, considering that two amino-groups are charged on the carbonyl nucleus; and if "thiocarbamide" is truly the diamide of thiocarbonic acid, and contains, therefore, the somewhat more acidic group $:CS$, the fact of its being less basic than urea is rendered intelligible.

For most substituted "thiocarbamides"—perhaps for all—the like arguments hold good. A hydrocarbon substituted derivative may yield the products to be expected from a thiourea, $RNH\cdot C(:NH)\cdot SH$ or $RN{:}C(NH_2)\cdot SH$, but there is every reason to believe that the compounds thus formulated, if existing by themselves, would show pronounced alkaline character, and would readily give salts with acids—which is contrary to experience, save in one or two exceptional cases. On the other hand, in such of their products as possess undoubtedly the thiourea structure, the basic character is manifest; even, sometimes, when an acidic radicle is included in the molecule; thus, benzyl "thiocarbamide" is neutral, whilst benzyl-ψ-thiourea, $NH_2\cdot C(:NH)\cdot S\cdot CH_2Ph$, is a well-marked base; the true thiohydantoins of the type  $CS<\begin{matrix}NH\cdot CO\\ NH\cdot CH_2\end{matrix}$ are neutral, whereas the *iso*-forms,  $NH{:}C<\begin{matrix}NH\cdot CO\\ S—CH_2\end{matrix}$, generally yield salts (less readily the more the iminic hydrogen atom is displaced by aryl radicles). There is no need to extend the catalogue, for, broadly speaking, the results follow always the lines here indicated.

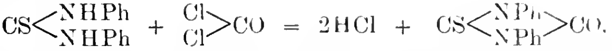
So far, then, as may be judged from the above considerations, "thiocarbamide," together with its monohydric substitution derivatives containing hydrocarbon radicles not attached to sulphur, has the configuration represented by the typical formula,

$$H_2N\cdot CS\cdot NH_2;$$

so long, at least, as these compounds remain in the static condition. It seems, moreover, highly probable that its corresponding acyl derivatives are similarly constituted; but the evidence available in the case of the latter is by no means so simple as that given above, nor is it so conclusive.

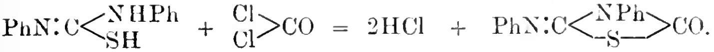
If it be reasonably certain that the substances variously named "thiocarbamides" or "thioureas" are, in fact, constituted on the symmetrical type just formulated; on the other hand, there is no doubt whatever that many of the interaction products contain the atomic complex, $NH_2\cdot C(:NH)\cdot SH$, of course, in a substituted form. To produce such new molecules, therefore, the parent substance in each case must have "behaved as if it were" a thiourea.

Thus, when thiocarbanilide reacts with carbonyl chloride, the product to be expected (for 2HCl is eliminated) is carbonylthiocarbanilide:



$$\mathrm{CS}<^{\mathrm{NHPh}}_{\mathrm{NHPh}} + {}^{\mathrm{Cl}}_{\mathrm{Cl}}>\mathrm{CO} = 2\mathrm{HCl} + \mathrm{CS}<^{\mathrm{NPh}}_{\mathrm{NPh}}>\mathrm{CO}.$$

but the product of this reaction, although called "carbonylthiocarbanilide," is an isomeride of that substance, the diphenylthiocarbamide "behaving as if it were" diphenylthiourea:



$$\mathrm{PhN{:}C}<^{\mathrm{NHPh}}_{\mathrm{SH}} + {}^{\mathrm{Cl}}_{\mathrm{Cl}}>\mathrm{CO} = 2\mathrm{HCl} + \mathrm{PhN{:}C}<^{\mathrm{NPh}}_{\mathrm{S}}>\mathrm{CO}.$$

Similarly, a monohydric thiocarbamide, $RNH\cdot CS\cdot NH_2$, when treated with chloroacetic acid, or with chloroacetyl chloride, yields, not the thiohydantoin,

$$\mathrm{CS}<^{\mathrm{NR\cdot CH_2}}_{\mathrm{NR\cdot CO}}, \quad \text{or} \quad \mathrm{CS}<^{\mathrm{NR-CO}}_{\mathrm{NH\cdot CH_2}},$$

which might be expected, but instead the *iso*thiohydantoin,

$$\mathrm{RN{:}C}<^{\mathrm{NH\cdot CO}}_{\mathrm{S-\!\!-CH_2}}.$$

Now, the former class of substances is represented by many members, which are quite stable, showing no tendency to undergo transformation into compounds of the latter class. Consequently, the *iso*thiourea derivative does not result through desmotropic change of a normal derivative initially formed; it is clearly an original product, and in this sense the statement is justifiable that the parent thiocarbamide has behaved as a thiourea. Whether, in such reactions, a thiocarbamide actually changes into a thiourea is a different issue, and will presently be considered.

In the foregoing portion of this paper we have confined ourselves almost exclusively to the statement and discussion of facts and views already published; the remainder includes a description of our own most recent work, and its bearing on certain of the above-mentioned problems.

EXPERIMENTAL.

Benzoyl Chloride and Thiocarbanilide.

A compound of these substances, in molecular proportion, was produced by dissolving them in acetone, and concentrating the solution in a vacuum; the nearly white solid melted, with evolution of hydrogen chloride, at 112—113°, and gave on analysis the following result:

0·577, fused with $NaOH+KNO_3$, required 15·2 c.c. $N/10$-$AgNO_3$. Cl = 9·35.

$C_{20}H_{17}ON_2ClS$ requires Cl = 9·63 per cent.

The additive compound, when heated with alcohol to 40°, changed suddenly to a felted mass of very slender needles, devoid of chlorine; these were dissolved by further gentle warming; on cooling, the solution (which now had a slight odour of ethyl benzoate) deposited tufts of slender, pale lemon-yellow prisms. The product, in alcohol, was readily desulphurised by alkaline salts of lead or of silver, and a sulphur determination gave the figures for a monobenzoylated diphenylthiocarbamide:

0·3475 gave 0·240 $BaSO_4$. S = 9·49.

$C_{20}H_{16}ON_2S$ requires S = 9·63 per cent.

Alcohol, therefore, had removed from the additive compound the elements of hydrogen chloride. This change occurs very readily; for example, by mere contact with cold water, or by addition of the latter to the acetone solution.

At 113° the yellow thiocarbamide melted to a colourless liquid, which soon began to deposit long, colourless prisms; when freed, by means of light petroleum, from the liquid portion, they were found to consist of benzanilide. The petroleum extract had the odour of phenylthiocarbimide, and when mixed with aniline yielded thiocarbanilide. Consequently, the change on fusion occurs as follows:

$$PhNH\cdot CS\cdot NPh\cdot COPh = PhNCS + PhCO\cdot NHPh.$$

When boiled with water, or even by continued heating of its solution in alcohol, the compound undergoes the same change; it is desirable, therefore, in recrystallising from the latter solvent, to keep the temperature below the boiling point and to operate quickly.

Phenylthiocarbimide and benzanilide failed to unite, either on gentle warming or after remaining in contact for six months in the cold.

Cold, dilute alkali (one equivalent) failed smoothly to de-benzoylate the thiocarbamide, the alcoholic mixture slowly decomposing, with formation of phenylthiocarbimide, thiocarbanilide, and benzanilide. Concentrated hydrochloric acid, however, when warmed with the solid, gave thiocarbanilide and benzoic acid, together with a trace of phenylthiocarbimide, the latter originating, perhaps, through the action of the strong acid on the first-named product.

A special interest attached to the result of this de-benzoylation. For, if it occurs by direct exchange of hydrogen for benzoyl, the product to be expected from benzoylthiocarbanilide is that which was obtained, namely, thiocarbanilide; whereas, if the benzoyl compound were of the form PhCO·NPh·C(:NPh)·SH one might expect, as product, the hitherto unknown substance,

PhNH·C(:NPh)·SH,

isomeric with thiocarbanilide.

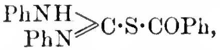
In the benzoyl chloride additive compound the elements of hydrogen chloride are readily available. Warming, or mere contact with alcohol, or with water, suffices to decompose the product; but not into the constituents to be expected from a molecular compound; on the contrary, the readiness with which it gives up chlorine, whilst retaining the benzoyl group, suggests that in the primary combination these radicles have already become separated.

Regarding the essential nature of that primary combination, the results of the following experiments appear to be significant.

Cold concentrated hydrochloric acid has little or no action on the benzoyl chloride additive compound (water alone, as previously mentioned, withdraws the elements of hydrogen chloride). Benzoylthiocarbanilide was allowed to remain for several hours in contact with concentrated hydrochloric acid in large excess: no change took place. Dry hydrogen chloride was passed, in large excess, through solutions of benzoylthiocarbanilide in acetone and in chloroform; liquids in which the benzoyl chloride additive compound is sparingly soluble or insoluble. At no stage of the operation did any solid matter appear; and from the chloroform solution, by evaporation of the solvent, the whole of the dissolved thiocarbamide was recovered unchanged. Whilst, therefore, the additive compound behaves as though it were a hydrochloride of benzoylthiocarbanilide, on the other hand, the latter compound, once formed, appears to be incapable of uniting with cold hydrochloric acid to regenerate the substance from which it was produced. Neither does heating facilitate the union; contrariwise, it withdraws the benzoyl radicle from the benzoylated thiocarbamide.

From these results it may reasonably be inferred that the organic complex contained in the additive compound of benzoyl chloride with thiocarbanilide is not benzoyldiphenylthiocarbamide, but an isomeric form of the latter; and since that form is basic enough to be able to retain the elements of an acid, there can be little doubt that the benzoyl group is attached directly to the sulphur atom of the original thiocarbanilide (see also Dixon and Hawthorne, Trans., 1907, **91**, 144; Dixon and Taylor, *ibid.*, 1908, **93**, 26).

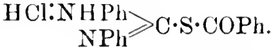
Accordingly, the outline configuration of this isomeric complex may be represented by the constitutional formula,



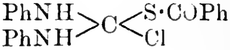
$$\begin{array}{r}\mathrm{PhNH}\\ \mathrm{PhN}\end{array}\!\!>\!\mathrm{C{\cdot}S{\cdot}COPh},$$

the elements of a molecule of hydrogen chloride being also contained in the system; when these are eliminated the benzoyl radicle leaves the sulphur and becomes joined to nitrogen.*

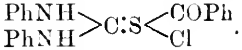
There are many ways in which these elements might conceivably be held; apart from such as are manifestly improbable, three demand consideration:

I. 

$$\begin{array}{r}\mathrm{HCl{:}NHPh}\\ \mathrm{NPh}\end{array}\!\!>\!\mathrm{C{\cdot}S{\cdot}COPh}.$$

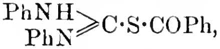
II. 

$$\begin{array}{r}\mathrm{PhNH}\\ \mathrm{PhNH}\end{array}\!\!>\!\mathrm{C}\!<\!\begin{array}{l}\mathrm{S{\cdot}COPh}\\ \mathrm{Cl}\end{array}$$

III. 

$$\begin{array}{r}\mathrm{PhNH}\\ \mathrm{PhNH}\end{array}\!\!>\!\mathrm{C{:}S}\!<\!\begin{array}{l}\mathrm{COPh}\\ \mathrm{Cl}\end{array}.$$

Form (I) has little to commend it; for if benzoyl cannot remain combined with sulphur to yield the free molecule,



$$\begin{array}{r}\mathrm{PhNH}\\ \mathrm{PhN}\end{array}\!\!>\!\mathrm{C{\cdot}S{\cdot}COPh},$$

it can scarcely be supposed that the union of hydrogen chloride with one of the nitrogen atoms would produce a more stable molecule. As regards (II) the case is somewhat similar; if the acyl radicle is not of itself disposed to remain attached to bivalent sulphur, it is not easy to understand how the presence of a chlorine atom at the neighbouring carbon atom could serve to increase the attraction between benzoyl and sulphur. Formula (III), however, is essentially different; for here the sulphur is represented as exerting four-fold valence, the whole molecule thus constituting a kind of sulphonium chloride. In the ordinary sulphonium compounds the salinity or basicity, as the case may be, is developed, out of constituents not in themselves exhibiting such characters, through the increased valency of the sulphur. In like manner, the alkylogens, uniting with thiocarbamides, yield well-marked saline products, whence bases may be obtained, in which sulphur and the alkyl radicle are undoubtedly conjoined. The latter bases, however, are not hydroxy-derivatives of the corresponding chlorides, but result through loss of the elements of a molecule of haloid acid; and hence the sulphur is no more than bivalent. Here the basicity of the residue cannot be attributed to the quadrivalence of sulphur; nor is it likely to be due to the engagement of the latter with an alkyl radicle.† The union of the alkyl radicle with the sulphur

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* The additive compound, when de-benzoylated by means of warm, concentrated hydrochloric acid, yielded the same products as those obtained from benzoylthiocarbanilide, namely, thiocarbanilide and benzoic acid

† See footnote, p. 2509.

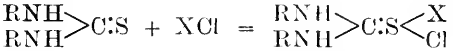
atom, however, necessitates the existence of a ψ-thiourea form (for example, EtNH·C(:NEt)·SAlk); and, as previously mentioned, configurations of such a type seem always to manifest a strongly basic character. In the case of ψ-thioureas, therefore, the basicity is probably due, not to the fact that sulphur is engaged with an alkyl radicle, but to the configuration of the whole molecule. On the other hand, the salinity of the original additive compound is not necessarily due to the combination of such a molecule with an acid, but may be conditioned entirely through the development of quadrivalence by the sulphur atom. Moreover, although the ψ-thioureas can unite again with the haloid acid, it is not yet certain how the two combine.

A well-marked electronegative radicle, however, apparently cannot by itself remain attached to the thiocarbamidic sulphur atom when this is bivalent; that is, the type of compound,

$$H_2N\cdot C(:NH)\cdot SX,$$

is essentially unstable, and there does not appear to be any reason why conjugation with a molecule of haloid acid should render it stable.

The view of the constitution of such substances, now proposed, does not, however, regard them as hydrochlorides, etc.; we suggest that the sulphur becoming quadrivalent can unite with the separated constituents of even a strongly-marked acid chloride, R·COCl. According to this view, the thiocarbamide molecule undergoes no tautomeric change, but unites directly with the acyl (or alkyl) haloid; for example:



$$\begin{matrix}RNH\\RNH\end{matrix}{>}C{:}S + XCl = \begin{matrix}RNH\\RNH\end{matrix}{>}C{:}S{<}\begin{matrix}X\\Cl\end{matrix}.$$

When from such a molecule the elements of haloid acid are withdrawn, the valency of the sulphur falls back to normal:

$$\begin{matrix}RNH\\RNH\end{matrix}{>}C{:}S{<}\begin{matrix}X\\Cl\end{matrix} = HCl + \begin{matrix}RNH\\RN\end{matrix}{\geqslant}C\cdot SX,$$

whereupon the acyl radicle, feebly held by the bivalent sulphur, moves to the unsaturated nitrogen atom, thus:

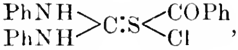
$$\begin{matrix}RNH\\RN\end{matrix}{\geqslant}C\cdot SX \longrightarrow \begin{matrix}RNH\\RNX\end{matrix}{>}C{:}S.$$

An alkyl radicle, however, not being disposed readily to part from the sulphur, remains attached, the group RN: therefore becoming doubly linked to the carbon:

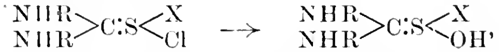
$$\begin{matrix}RNH\\RN\end{matrix}{>}C\cdot S\cdot Alk \longrightarrow \begin{matrix}RNH\\RH\end{matrix}{\geqslant}C\cdot S\cdot Alk.$$

Later on, other facts will be adduced, which appear to support the view here advanced; meanwhile, it may be pointed out that the mechanism suggested is consistent with the observation, recorded above, that *ab*-diphenylthiocarbamide (and not the isomeric thiourea) is produced alike by the de-benzoylation of benzoyldiphenylthiocarbamide and of the additive compound of benzoyl chloride with thiocarbanilide.

So far as the former is concerned, if it is truly a thiocarbamide, PhCO·NPh·CS·NHPh, the product to be expected is that which is formed, namely, *ab*-diphenylthiocarbamide. As regards the latter additive compound, however, it is different; for, as mentioned above, the product to be expected from a compound having the benzoyl radicle attached to sulphur is PhNH·C(:NPh)·SH,HCl, or else the free "base," PhNH·C(:NPh)·SH. This, of course, could conceivably transform itself by tautomeric or desmotropic rearrangement into thiocarbanilide; but the assumption that it does so is just as gratuitous as the assumption that thiocarbanilide changes itself into diphenylthiourea.

According to the view of quadrivalent sulphur, there is no difficulty; the product,  $\begin{matrix}\mathrm{PhNH}\\ \mathrm{PhNH}\end{matrix}\!>\!\mathrm{C{:}S}\!<\!\begin{matrix}\mathrm{COPh}\\ \mathrm{Cl}\end{matrix}$, either loses benzoyl chloride by the direct elimination of its elements, or, more probably, the elements of hydrogen chloride are first removed, whereupon the benzoyl radicle, passing to the unsaturated nitrogen atom, yields benzoyldiphenylthiocarbamide, which, in turn, is de-benzoylated. Whether, however, the benzoyl is removed directly or indirectly, *ab*-diphenylthiocarbamide must be the product; and there is no need, in any case, to assume that tautomeric change has occurred.

The mechanism by which such compounds lose the elements of hydrogen chloride probably operates in two stages. Mere dissolution in the cold by a non-hydrolysing solvent has no effect in producing hydrogen chloride; but this is eliminated in presence of various hydrolysts. These facts may adequately be explained by supposing that the hydrolyst converts the haloid derivative into the corresponding hydroxide:



$$\begin{matrix}\mathrm{NHR}\\ \mathrm{NHR}\end{matrix}\!>\!\mathrm{C{:}S}\!<\!\begin{matrix}\mathrm{X}\\ \mathrm{Cl}\end{matrix} \longrightarrow \begin{matrix}\mathrm{NHR}\\ \mathrm{NHR}\end{matrix}\!>\!\mathrm{C{:}S}\!<\!\begin{matrix}\mathrm{X}\\ \mathrm{OH}\end{matrix},$$

from which a molecule of water is eliminated, the acyl radicle thereupon moving to the nitrogen to take the place of the hydrogen which the latter has surrendered.

In many cases dry fusion leads to the production of hydrogen chloride (with concomitant transference of the acyl radicle from sulphur to nitrogen); in these circumstances the union of hydrogen with chlorine is probably direct.

Acetyl Chloride and Thiocarbanilide.

Deninger states (*Ber.*, 1895, **28**, 1322) that thiocarbanilide cannot be acetylated by the Schotten-Baumann method. Similarly, when dilute alkali was added to the compound $CS(NHPh)_2,Me\cdot COCl$, the acyl chloride was withdrawn, thiocarbanilide being left (Dixon and Hawthorne, *loc. cit.*).

Nevertheless, by a slight alteration of the conditions it is possible to transfer the acetyl radicle to one of the nitrogen atoms. The operation was conducted as follows: To thiocarbanilide enough acetone was added thoroughly to moisten it; the mixture, warmed on the water-bath, was treated with a trifle more than the calculated amount of acetyl chloride, and stirred until it became clear. The resultant syrup was poured into excess of dilute alkali, whereupon a pasty solid was formed, consisting partly of unchanged thiocarbanilide. This having been removed by filtration, the filtrate was acidified, an oil thus being precipitated, which on stirring gradually became solid. The solid, on recrystallisation from alcohol, was obtained in fine, brilliant, vitreous, apparently rhombic prisms; they melted at 90—90·5° (corr.), and, after another recrystallisation, at the same temperature. Deninger gives the melting point of acetyldiphenylthiocarbamide as 91°, his compound having been prepared by crystallising from alcohol a supposed diacetyldiphenylthiocarbamide. Hugershoff, by the direct action of acetic anhydride on thiocarbanilide, obtained (*loc. cit.*) an acetyl derivative, to which he assigns the melting point 96°.*

Acetylthiocarbanilide is insoluble in water, but decomposes when boiled with it, yielding phenylthiocarbimide and acetanilide; it is moderately freely soluble in hot alcohol, rather sparingly so in cold. The alcoholic solution yields with alcoholic silver nitrate a white precipitate; on warming, this dissolves, and soon desulphurisation takes place. If, however, ammoniacal silver nitrate is used, the white precipitate is scarcely affected, even by boiling. With alkaline solution of lead, desulphurisation occurs very readily on warming.

Benzoyl Chloride and Benzoyl-ab-*diphenylthiocarbamide.*

Since acylated thiocarbamides show little or no tendency to unite directly with acyl haloids (Dixon and Hawthorne, *loc. cit.*), a direct combination of the above materials was scarcely to be anticipated.

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* A preparation, made by us, according to his instructions, liquefied at about 90°. The liquefaction is not, however, a true fusion; it is a decomposition, and the temperature at which it occurs depends much on the duration of the preliminary heating.

Nevertheless, Deninger, by a modification of the Schotten-Baumann method, succeeded (*loc. cit.*) in producing dibenzoyldiphenylthiocarbamide, CS(NPh·COPh)$_2$—apparently the only known example of a thiocarbamide containing two acyl radicles. We have repeated the preparation according to his instructions, and have further verified by analysis (he gives no estimation of sulphur) the accuracy of his observations:

0·872 (Kjeldahl) required 38·7 c.c. $N/10$-H_2SO_4. N = 6·24.
0·505 gave 0·280 $BaSO_4$. S = 7·64.
$C_{27}H_{20}O_2N_2S$ requires N = 6·42; S = 7·34 per cent.

To learn whether, by this method, the above monobenzoyldiphenylthiocarbamide could further be benzoylated so as to produce Deninger's compound, the former, dissolved in warm pyridine, was mixed with a trifle more than 1 molecular proportion of benzoyl chloride. That the change anticipated had taken place seemed probable, for the solution became bright orange (a phenomenon which occurs in the preparation of the dibenzoyl compound). The addition of water, followed by hydrochloric acid, yielded a tenacious paste; by recrystallisation from alcohol this gave bright, orange-yellow needles, melting at 161—162° (corr.), and showing all the properties of Deninger's compound (he records the melting point as 160·5°).

Curiously enough, the latter compound shows considerable stability, and does not appear to suffer change, even by somewhat prolonged boiling with alcohol, in which it is sparingly soluble. In order to learn whether, by elimination of one of the acyl radicles, monobenzoyldiphenylthiocarbamide would be regenerated, the alcoholic solution was treated with 1 equivalent of sodium, previously dissolved in alcohol, the mixture being allowed to evaporate spontaneously at the temperature of the room. In this way, white crystals were obtained, devoid of sulphur, melting at 160—161°, and consisting of benzanilide. It seems probable that monobenzoyldiphenylthiocarbamide is first produced, and decomposes on long contact with alcohol into benzanilide and phenylthiocarbimide; the latter, in turn, uniting with the alcohol to form the easily soluble phenylthiourethane.

In connexion with the above result it may be recalled that Deninger was unable, by the method he employed, to obtain monobenzoyldiphenylthiocarbamide; this is due, no doubt, to the fact that the dibenzoyl compound obtained by him is fairly stable, whereas the monobenzoyl derivative, as we have shown above, is distinctly unstable.

Acetyl Chloride and Benzoyldiphenylthiocarbamide.

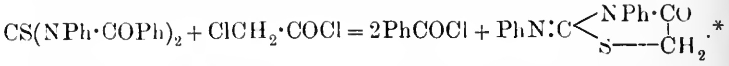
The further benzoylation of the above-named thiocarbamide having been accomplished by Deninger's method, the corresponding acetylation might be expected to follow as a matter of course. The pyridine solution, in fact, when mixed with acetyl chloride, became deep yellow—just as in the benzoylation—and, in like manner, an oil resulted. On treatment with alcohol, however, the orange-yellow colour was destroyed, and the resultant pale yellow needles melted at 113°, and proved to consist of benzoyldiphenylthiocarbamide. This observation harmonises with another of Deninger's, for he appears to have succeeded in producing diacetyldiphenylthiocarbamide (by treating thiocarbanilide in pyridine with acetyl chloride). The material obtained by crystallisation from alcohol, however, proved to be monoacetyldiphenylthiocarbamide, a fact which he attributes to the elimination, by the solvent, of the second acetyl radicle. It is curious that, whilst dibenzoyldiphenylthiocarbamide is more stable, in contact with hot alcohol, than is the monobenzoyl compound, the diacetyl and the acetylbenzoyl derivatives should so readily undergo decomposition.

Chloroacetyl Chloride and Dibenzoyldiphenylthiocarbamide.

Recent observations having shown (Dixon and Taylor, this vol., p. 558) that mono-acyl substituted thiocarbamides react with chloroacetyl chloride, by loss of the acyl radicle, thereby yielding the corresponding *iso*thiohydantoins, the question naturally arose whether Deninger's dibenzoyldiphenylthiocarbamide would be attacked by chloroacetyl chloride. In this case there is no SH-group available, and consequently, an *iso*thiohydantoin, if produced at all, cannot acquire the characteristic linking $\cdot S\cdot CH_2\cdot CO\cdot$ through the combination of the SH-hydrogen with the chlorine of the group $ClCH_2\cdot$.

When the above-named tetrasubstituted thiocarbamide, dissolved in acetone (in which it is readily soluble), was mixed with 1 molecular proportion of chloroacetyl chloride, the odour of benzoyl chloride quickly became perceptible; the solution was then concentrated by evaporation in a vacuum at the ordinary temperature. Rosettes of white needles were thus obtained, containing chlorine, and melting between 180° and 183°; they responded to Andreasch's iron-test for thiolacetic acid (*Ber.*, 1879, **12**, 1385), and by recrystallisation from alcohol—which eliminated hydrogen chloride—were changed into white plates melting at 176—177° (corr.), and consisting of Lange's (*Ber.*, 1879, **12**, 595) diphenyl-*iso*thiohydantoin. The acetone-filtrate, on treatment with aniline, lost the odour of benzoyl chloride, and yielded a white solid; this, when recrystallised from alcohol, was recognised by its melting point (158—159°, uncorr.), appearance, and properties as benzanilide.

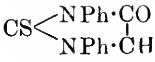
Hence, the reaction had taken place as follows:



$$\mathrm{CS(NPh{\cdot}COPh)_2 + ClCH_2{\cdot}COCl = 2PhCOCl + PhN{:}C}{<}\begin{matrix}\mathrm{NPh{\cdot}CO}\\ \mathrm{S{-}{-}{-}CH_2}\end{matrix}.^*$$

This result is noteworthy; for whilst, on the one hand, the thiocarbamide molecule neither contains the SH-group, nor can by any transposition furnish it, yet, on the other hand, the correctness of the formula assigned to Lange's diphenyl*iso*thiohydantoin is thoroughly well established.

Consistently with our present ideas, there appear to be only four possible ways of accounting for the production of the last-named substance by this particular method: (i) A true thiohydantoin,



$\mathrm{CS}{<}\begin{matrix}\mathrm{NPh{\cdot}CO}\\ \mathrm{NPh{\cdot}CH_2}\end{matrix}$, first results, and subsequently changes into the *iso*-form; (ii) the supposed "thiocarbamide" is really a ψ-thiourea,

$\mathrm{PhN{:}C}{<}\begin{matrix}\mathrm{NPh{\cdot}COPh}\\ \mathrm{S{\cdot}COPh}\end{matrix}$, (iii) the thiocarbamide, before reacting with the chloroacetyl chloride, undergoes transformation into the above ψ-thiourea; (iv) the thiocarbamide unites as such with the chloroacetyl chloride, the product subsequently decomposing in such a way as to yield the *iso*thiohydantoin.

Of these possibilities, (i) may be dismissed forthwith, for the true thiohydantoins are known, and show no tendency to such change. No. (ii), although not flatly contradicted by any known facts, is plainly improbable; for, if the acyl radicle cannot remain conjoined with sulphur to form the molecule

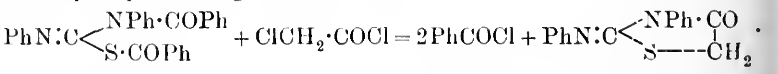
$$\mathrm{PhNH{\cdot}C({:}NPh)S{\cdot}COPh},$$

there is little reason to believe that the configuration,

$$\mathrm{PhN(COPh){\cdot}C({:}NPh){\cdot}S{\cdot}COPh},$$

would be capable of existence.

In case (iii) it is conceivable (in fact, it represents the kind of explanation commonly advanced) that, under the attack of chloroacetyl chloride, a molecule, previously existing as $\mathrm{CS(NPh{\cdot}COPh)_2}$, might undergo tautomeric deformation into a ψ-thiourea, the action thereupon proceeding on the lines:

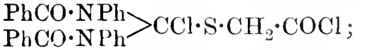


$$\mathrm{PhN{:}C}{<}\begin{matrix}\mathrm{NPh{\cdot}COPh}\\ \mathrm{S{\cdot}COPh}\end{matrix} + \mathrm{ClCH_2{\cdot}COCl = 2PhCOCl + PhN{:}C}{<}\begin{matrix}\mathrm{NPh{\cdot}CO}\\ \mathrm{S{-}{-}{-}CH_2}\end{matrix}.$$

---

[*] This compound, when prepared from chloroacetyl chloride, tends to separate in the form of a hydrochloride, which is dissociated by hot alcohol from the conjoined acid. In the case mentioned above, the hydrochloric acid originally present comes probably from the action of moisture on the liberated benzoyl chloride.

Such a view, however, conflicts with the experimental results mentioned earlier in the present paper; an acyl radicle, it appears, is strongly disposed to move from sulphur to nitrogen, but never shows any tendency to the reverse movement. Where a hydrogen atom is concerned, its relative lightness, its well-known mobility, and the indifference with which it can associate itself with electropositive or electronegative groups, may possibly be invoked as reasons to account for its wanderings; but with the benzoyl complex the case is different. Benzoyl is neither light, nor, in most circumstances, remarkably mobile; its electronegative character is distinctly marked; and there is some difficulty in supposing that it migrates from a comparatively electropositive and stable position, at nitrogen, to one that is electronegative, at sulphur, for the express purpose (if one may put it so) of producing free benzoyl chloride.

Case (iv) remains to be considered; that is, a direct union between the constituents, with subsequent decomposition of the resultant additive compound. Here the fractions of the chloroacetyl chloride are necessarily $Cl\cdot$ and $\cdot CH_2\cdot COCl$, the latter of which must be engaged with the sulphur atom; the $Cl\cdot$, however, may be conjoined with the sulphur, through the development of quadrivalency on its part, or to carbon, through the opening up of the double bond of the thiocarbonyl group. In the former case the combination would be  $\begin{matrix}\mathrm{PhCO{\cdot}NPh}\\ \mathrm{PhCO{\cdot}NPh}\end{matrix}\!>\!\mathrm{C{:}S}\!<\!\begin{matrix}\mathrm{Cl}\\ \mathrm{CH_2{\cdot}COCl}\end{matrix}$; in the latter,  $\begin{matrix}\mathrm{PhCO{\cdot}NPh}\\ \mathrm{PhCO{\cdot}NPh}\end{matrix}\!>\!\mathrm{CCl{\cdot}S{\cdot}CH_2{\cdot}COCl}$; and from either of them, by loss of two molecules of benzoyl chloride, Lange's diphenyl*iso*thiohydantoin would be produced.

Although, so far as the genesis of this substance is concerned, there is nothing to choose between the two configurations given above, yet the balance of probability seems to lie in favour of the first, for, by the development of the quadrivalency of the sulphur atom, some reason at least can be found to explain why this element should tend to unite with a markedly electronegative radicle; whereas, so far as may be judged from the facts already noted regarding the combinations of acid chlorides, there is little or no ground for supposing that bivalent sulphur would attract the radicle $CH_2\cdot COCl$ (see Dixon and Taylor, this vol., p. 568), especially in a diacyl-substituted thiocarbamide.

Benzoyl Chloride and Diphenylmethylthiocarbamide.

In order to learn whether a trisubstituted thiocarbamide can unite with an acyl chloride, and, if so, whether the combined acyl radicle is transferable to a nitrogen atom with production of a tetrasubstituted thiocarbamide, the following experiments were made.

ab-Diphenyl-*a*-methylthiocarbamide, MeNPh·CS·NHPh, and benzoyl chloride, in molecular proportions, were separately dissolved in acetone, and the solutions mixed. By concentration, a white, apparently amorphous solid was obtained, melting at 98—99° with evolution of hydrogen chloride; the solid was insoluble in water, but when heated with the latter yielded a solution of hydrogen chloride.

0·7375 Gram was boiled with water; the clear solution, filtered from the insoluble residue, required for neutralisation 19·0 c.c. *N*/10-alkali. Cl = 9·15:

0·6015, fused with $NaOH + KNO_3$, required 15·8 c.c. *N*/10-$AgNO_3$. Cl = 9·32.

0·330, fused as above, gave 0·200 $BaSO_4$. S = 8·32.

$C_{21}H_{19}ON_2ClS$ requires Cl = 9·28; S = 8·37 per cent.

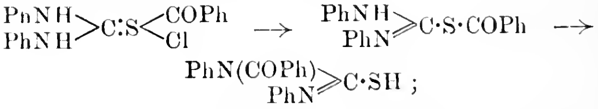
Consequently, the substance was a molecular additive product of the materials used.

By recrystallisation from boiling alcohol, cream-white prisms were obtained, devoid of chlorine, and melting at 130—131°. The substance was very stable towards alkaline solution of lead, being desulphurised only near the fusion point of the mixture; a sulphur determination showed it to be the tetrasubstituted compound *benzoyldiphenylmethylthiocarbamide*, PhCO·NPh·CS·NMePh:

0·3756 gave 0·256 $BaSO_4$. S = 9·36.

$C_{21}H_{18}ON_2S$ requires S = 9·25 per cent.

This particular experiment was made especially with the object of learning whether the transposition of the acyl radicle occurs simply on the withdrawal of the elements of hydrogen chloride from the additive compound, or by exchange of hydrogen for the acyl radicle. For, in the cases previously cited, the action might take place on lines such as the following:



$$\begin{matrix}\mathrm{PhNH}\\\mathrm{PhNH}\end{matrix}\!>\!\mathrm{C{:}S}\!<\!\begin{matrix}\mathrm{COPh}\\\mathrm{Cl}\end{matrix}\;\rightarrow\;\begin{matrix}\mathrm{PhNH}\\\mathrm{PhN}\end{matrix}\!\geqslant\!\mathrm{C\cdot S\cdot COPh}\;\rightarrow\;\begin{matrix}\mathrm{PhN(COPh)}\\\mathrm{PhN}\end{matrix}\!\geqslant\!\mathrm{C\cdot SH};$$

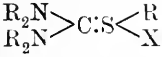
whereas, in the case now tested, an exchange of hydrogen for benzoyl cannot occur:

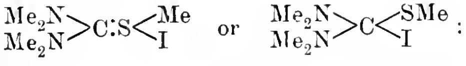
$$\begin{matrix}\mathrm{PhNMe}\\\mathrm{PhNH}\end{matrix}\!>\!\mathrm{C{:}S}\!<\!\begin{matrix}\mathrm{COPh}\\\mathrm{Cl}\end{matrix} = \mathrm{HCl} + \begin{matrix}\mathrm{PhNMe}\\\mathrm{PhN}\end{matrix}\!\geqslant\!\mathrm{C\cdot S\cdot COPh};$$

and hence, if the benzoyl radicle migrates from sulphur to nitrogen (which appears to be the case), it must do so directly, and not through any transposition by which a thiourea could be produced. That is:

$$\begin{matrix}\mathrm{PhNMe}\\ \mathrm{PhN}\end{matrix}\!\geqslant\mathrm{C{\cdot}S{\cdot}COPh}\ \longrightarrow\ \begin{matrix}\mathrm{PhNMe}\\ \mathrm{PhN(COPh)}\end{matrix}\!>\mathrm{C{:}S}.$$

The view now advanced, namely, that the transformations undergone by thiocarbamides under the influence of various halogen-containing substances are due to the preliminary formation of additive compounds, through the development of the quadrivalency of the sulphur atom of the thiocarbamide, may, of course, need revision in the light of further experience. Meanwhile, however, it has the advantage of furnishing an intelligible working principle, as a substitute for the customary assumptions of tautomeric rearrangement of thiocarbamide molecules into thiourea configurations (or vice versa), acquired beforehand for the purpose of allowing certain reactions to take place. There does not appear to be any experimental evidence to show that such changes really occur; moreover, as pointed out above, the genesis of Lange's diphenyl*iso*thiohydantoin from dibenzoyldiphenylthiocarbamide—save by the making of assumptions warranted by no known facts—cannot be reconciled with the idea of such tautomeric change.

If the interaction products originate through the decomposition of additive compounds in which the sulphur of thiocarbamide has developed quadrivalence, one might foresee the possibility of obtaining, from thiocarbamides fully substituted by radicles not so prone to elimination as hydrogen or acyl groups, compounds of the form  $\begin{matrix}\mathrm{R_2N}\\ \mathrm{R_2N}\end{matrix}\!>\mathrm{C{:}S}\!<\!\begin{matrix}\mathrm{R}\\ \mathrm{X}\end{matrix}$ (X = halogen). Attempts to combine tetraphenylthiocarbamide in warm acetone with acetyl chloride, or with benzoyl chloride, proved unsuccessful; and we were preparing to repeat the experiments, with a tetra-substituted thiocarbamide containing radicles less electronegative than phenyl, when we happened, fortunately, on a paper by Delépine, which had previously escaped our notice; here, to some extent, at least, the question raised found its answer. Delépine records (*Bull. Soc. chim.*, 1910, [iv], **7**, 991) that tetramethylthiocarbamide, in ether, unites slowly with methyl iodide to form a compound, $\mathrm{CS(NMe_2)_2,MeI}$, which, with one molecular proportion of silver nitrate, yields the corresponding "nitromethylate," and with more silver nitrate and ammonia gives silver methyl mercaptide. Hence, the methyl of the methyl iodide used is combined directly with the sulphur, the additive product being either



$$\begin{matrix}\mathrm{Me_2N}\\ \mathrm{Me_2N}\end{matrix}\!>\mathrm{C{:}S}\!<\!\begin{matrix}\mathrm{Me}\\ \mathrm{I}\end{matrix}\quad \text{or}\quad \begin{matrix}\mathrm{Me_2N}\\ \mathrm{Me_2N}\end{matrix}\!>\mathrm{C}\!<\!\begin{matrix}\mathrm{SMe}\\ \mathrm{I}\end{matrix}:$$

between these two constitutions he does not attempt to decide. In view of this synthesis, we did not think it necessary to pursue our experiments, it being now clear that even the complete substitution of all the hydrogen atoms of a thiocarbamide does not destroy its power of further union with an alkyl haloid. The production of the "nitromethylate" is significant in showing the existence of basicity in a residue, the general configuration of which would not lead one to expect this phenomenon. If, however, the sulphur atom is quadrivalent, a reason for the basicity may be found. The mere accumulation of dimethylamino-groups is not alone sufficient to account for it, for tetramethylthiocarbamide, $Me_2N{\cdot}CS{\cdot}NMe_2$, is not a base.

In conclusion, a few cases may be given to illustrate how the mechanism of certain changes may be explained according to the views stated above, namely, that "thiocarbamide" and all its substitution derivatives containing monohydric radicles (except ψ-thioureas) are constituted on the one type $NH_2{\cdot}CS{\cdot}NH_2$, and that the derivation from such a symmetrical molecule of unsymmetrical or "thiourea" forms is caused, not through tautomeric change, but through the decomposition of additive products resulting from the parent thiocarbamides by the development on the part of the contained sulphur atom of a higher valency than it possesses in the uncombined thiocarbamides.

(i) *Alkyl or Acyl Haloid and a Thiocarbamide.*—Here, at first sight, an explanation of the formation of a ψ-thiourea might seem to lie, somehow, in the affinity of sulphur for an alkyl radicle. But, since the acyl radicle is by no means disposed to combine with dyad sulphur, and yet the acylogens, as well as the alkylogens, can unite with thiocarbamide, and with its mono-, di-, or tri-substitution derivatives, it is plain that the fact of combination must depend on something more than the attraction between the radicle and the sulphur atom. But if the presence of the haloid element tends to evoke the higher valence of the sulphur, the reluctance of the latter to combine with an acyl radicle may be diminished. That reluctance is not intense in any case, for, although thioacetic acid (for example) is very readily decomposable, it is capable of independent existence in ordinary circumstances.

With alkyl haloids, RX, and with acyl haloids, R·CO·X, the respective new molecules are:

$$(a)\ \begin{matrix}NH_2\\NH_2\end{matrix}\!\!>C{:}S\!<\!\begin{matrix}R\\X\end{matrix},\quad\text{and}\quad(b)\ \begin{matrix}NH_2\\NH_2\end{matrix}\!\!>C{:}S\!<\!\begin{matrix}CO{\cdot}R\\X\end{matrix}.$$

When from (*a*) the elements of HX are removed, the system $\begin{matrix}NH_2\\-NH\end{matrix}\!\!>C{:}S\!<^{R}$, originates; and since the union between sulphur and the alkyl radicle is strong, the parts (unless the whole complex decomposes, as may happen) maintain their existing positions; but as the radicle R cannot move to the nitrogen, the NH:-group becomes doubly linked to carbon, the two extra valencies of the sulphur, with the loss of halogen, ceasing to be active; this may be pictured as follows:

$$\substack{NH_2\\ -NH}\!>C{:}S\!<^{R} \longrightarrow \substack{NH_2\\ NH}\!\geqslant C\cdot S\!\lessdot^{R} \longrightarrow \substack{NH_2\\ NH}\!\geqslant C\cdot SR.$$

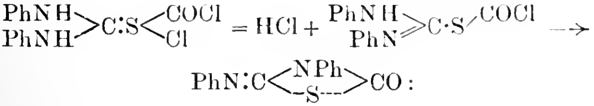
On the other hand, when HX is removed from (*b*), the resultant system, $\substack{NH_2\\ NH}\!\geqslant C\cdot S\cdot CO\cdot R$, weak by reason of the small attraction between S and R·CO·, readjusts itself more or less rapidly, the latter group transferring itself to the nitrogen atom, where it attains a position of stability.

That the molecule $NH_2\cdot C(:NH)\cdot S\cdot COR$ is not disposed towards stable existence, may be inferred from the fact that cyanamide with thioacetic acid, yields acetylthiocarbamide (Prätorius, *J. pr. Chem.*, 1880, [ii]. **21**, 147). Now, although in thioacetic acid the acetyl radicle is joined directly to sulphur, yet in acetylthiocarbamide this is not the case, for the latter compound is producible from acetylthiocarbimide and ammonia, and when desulphurised yields acetylcarbamide. In acetylthiocarbamide, therefore, it is certain that the acyl radicle is conjoined with a nitrogen atom; and hence the explanation of the reaction observed by Prätorius is most likely the following:

$$NH_2\cdot C{:}N + MeCO\cdot SH \longrightarrow NH_2\cdot C(:NH)\cdot S\cdot COMe \longrightarrow NH_2\cdot CS\cdot NH\cdot COMe.$$

This reaction is of interest as furnishing independent evidence that, in thiocarbamidic compounds, bivalent sulphur is incapable of retaining a well-marked electronegative radicle.

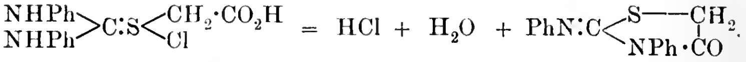
(ii) *Carbonyl Chloride and Thiocarbanilide.*—The product of the interaction of these substances, as previously mentioned, is not the symmetrical carbonyl derivative which might be expected, but has, instead, the configuration $PhN{:}C\!<\!\substack{NPh\\ \overline{S}}\!>\!CO$ (Will, *Ber.*, 1881, **14**, 1486). On the hypothesis that the sulphur becomes quadrivalent, thereby taking up the fractions ·Cl and ·COCl, the changes would run as follows:



$$\substack{PhNH\\ PhNH}\!>C{:}S\!<\!\substack{COCl\\ Cl} = HCl + \substack{PhNH\\ PhN}\!\geqslant C\cdot S\diagup^{COCl} \longrightarrow PhN{:}C\!<\!\substack{NPh\\ -S-}\!>\!CO:$$

A similar explanation holds, of course, for the compounds obtained with ethylene dibromide, or with chloroacetyl chloride or chloroacetic acid. In the last-named case, the elements of water are eliminated, as well as those of hydrogen chloride; but the reactions are all essentially the same; thus:

$$\begin{matrix}NPh\\NPh\end{matrix}\!>CS + \begin{matrix}CO_2H\\|\\CH_2Cl\end{matrix} = \begin{matrix}NHPh\\NHPh\end{matrix}\!>C{:}S<\begin{matrix}CH_2\cdot CO_2H\\Cl\end{matrix}, \text{ and}$$

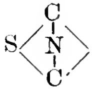


$$\begin{matrix}NHPh\\NHPh\end{matrix}\!>C{:}S<\begin{matrix}CH_2\cdot CO_2H\\Cl\end{matrix} = HCl + H_2O + PhN{:}C<\begin{matrix}S\text{---}CH_2\\ \quad\;\; |\\ NPh\cdot CO\end{matrix}.$$

(iii) *Penta-substituted Dithiobiurets.*—Billeter has shown (*Ber.*, 1893, **26**, 1688) that, by the union in the cold of dimethylthiocarbamyl chloride, $Me_2N\cdot CS\cdot Cl$, with ethylthiocarbanilide,

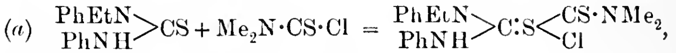
$$PhNEt\cdot CS\cdot NHPh,$$

a compound results, from which, by the elimination of the elements of hydrogen chloride, a base, $PhN{:}C(NPhEt)\cdot S\cdot CS\cdot NMe_2$, is obtained, melting at 89·8°; whereas, with phenylethylthiocarbamyl chloride, $PhNEt\cdot CS\cdot Cl$, and *b*-phenyl-*a*-dimethylthiocarbamide, $Me_2N\cdot CS\cdot NHPh$, the corresponding base melts at 91·2°. Each of these substances, if heated to 100° yields the same isomeride, melting at 98·8°, to which Billeter assigns, as most probable, the constitution, $PhN<\begin{matrix}CS\cdot NPhEt\\CS\cdot NMe_2\end{matrix}$. This formula, he suggests, might be the outcome of a transformation, in the course of which the atomic grouping



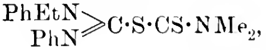
might occur as a transition-form.

On the lines mentioned above, the explanation is as follows:

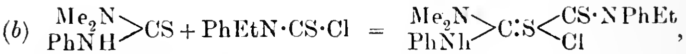


$$(a)\quad \begin{matrix}PhEtN\\PhNH\end{matrix}\!>CS + Me_2N\cdot CS\cdot Cl = \begin{matrix}PhEtN\\PhNH\end{matrix}\!>C{:}S<\begin{matrix}CS\cdot NMe_2\\Cl\end{matrix},$$

the latter, by loss of HCl, yielding

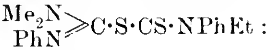


$$\begin{matrix}PhEtN\\PhN\end{matrix}\!\geqslant C\cdot S\cdot CS\cdot NMe_2,$$



$$(b)\quad \begin{matrix}Me_2N\\PhNH\end{matrix}\!>CS + PhEtN\cdot CS\cdot Cl = \begin{matrix}Me_2N\\PhNH\end{matrix}\!>C{:}S<\begin{matrix}CS\cdot NPhEt\\Cl\end{matrix},$$

the corresponding product from this being



$$\begin{matrix}Me_2N\\PhN\end{matrix}\!\geqslant C\cdot S\cdot CS\cdot NPhEt:$$

Billeter, although not in exactly the same way, arrives at the same constitutions for the two "bases" as those just given. Now the "bases" contain, charged on the sulphur atom in each case, the radicle $\cdot CS\cdot NMe_2$ or $\cdot CS\cdot NPhEt$; these are feebly electronegative, and hence do not tend very readily to pass from the sulphur. Nevertheless, they are electronegative (at least, as compared with alkyl radicles), and heat—as we have elsewhere shown—is a potent factor in displacing negative groups from sulphur to nitrogen in combinations of this kind. Accordingly, when the "bases" are heated, the usual transposition occurs, and, by migration of the substituted thiocarbamic group, there result, in case (*a*),

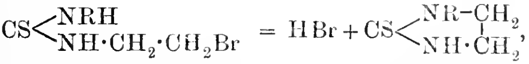
$$\mathrm{PhEtN\cdot CS\cdot NPh\cdot CS\cdot NMe_2},$$

and in case (*b*), $\mathrm{Me_2N\cdot CS\cdot NPh\cdot CS\cdot NPhEt}$, namely, forms that are identical.

(iv) *Compounds of Halogen-substituted Thiocarbimides with Bases, and of Halogen-substituted Bases with Thiocarbimides.*—Without giving details, or recalling the somewhat voluminous literature of the above subjects, it may suffice if we state the essential results of these actions—at least, as they commonly occur. In general, then, although specific cases are used in illustration, chloroacetylthiocarbimide, with a base, $\mathrm{R\cdot NH_2}$, does not yield the expected thiocarbamide, $\mathrm{CH_2Cl\cdot CO\cdot NH\cdot CS\cdot NHR}$, but instead a ring compound,  $\mathrm{RN{:}C}<\begin{array}{l}\mathrm{NH\cdot CO}\\ \mathrm{S{-}{-}CH_2}\end{array}$ (some kind of substituted *iso*thiohydantoin). In like manner, bromoethylamine, with a thiocarbimide, $\mathrm{R\cdot NCS}$, fails to furnish the thiocarbamide,

$$\mathrm{RNH\cdot CS\cdot NH\cdot CH_2\cdot CH_2Br},$$

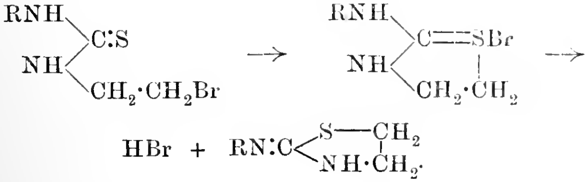
but gives instead a similar ring,  $\mathrm{RN{:}C}<\begin{array}{l}\mathrm{NH\cdot CH_2}\\ \mathrm{S{-}{-}CH_2}\end{array}$. That a molecule of haloid acid should be eliminated from either of these thiocarbamidic types is not surprising, for such a change could easily occur:



$$\mathrm{CS}<\begin{array}{l}\mathrm{NRH}\\ \mathrm{NH\cdot CH_2\cdot CH_2Br}\end{array} = \mathrm{HBr} + \mathrm{CS}<\begin{array}{l}\mathrm{NR{-}CH_2}\\ \mathrm{NH\cdot CH_2}\end{array},$$

The puzzle is, why it should fail to take place according to the equation given above. How does the methylene of the groups $\mathrm{\cdot CH_2Br}$ or $\mathrm{\cdot CH_2Cl}$, as the case may be, come into union with the sulphur atom?

If the sulphur atom becomes quadrivalent for the time being, the answer to this question is simple: the bromine, parting from the $\mathrm{\cdot CH_2Br}$, the constituents, as usual, add themselves to the sulphur; and when hydrogen bromide (or hydrogen chloride) is withdrawn, the valency of the sulphur, temporarily developed by the presence of the halogen element, falls back to normal, and the new ring has been produced:



$$\begin{array}{l}\mathrm{RNH}\\ \mathrm{NH}\end{array}\!\!>\mathrm{C{:}S}\ (\mathrm{NH}{-}\mathrm{CH_2\cdot CH_2Br}) \longrightarrow \begin{array}{l}\mathrm{RNH}\\ \mathrm{NH}\end{array}\!\!>\mathrm{C{=}SBr}\ (\mathrm{NH}{-}\mathrm{CH_2\cdot CH_2}{-}\mathrm{S}) \longrightarrow$$

$$\mathrm{HBr} + \mathrm{RN{:}C}<\begin{array}{l}\mathrm{S{-}{-}CH_2}\\ \mathrm{NH\cdot CH_2}\end{array}.$$

Although in some of the cases cited above there seems to be little room for doubting the quadrivalence of the sulphur atom, yet in none is direct proof of the phenomenon available. In the hope of securing this, we propose to make further experiments.

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CCLXII.—*The Influence of Sodium Salts of Organic Acids on the Rate of Hydrolysis by Alkali.*

By GEORGE SENTER and FRITZ BULLE.

THE remarkable accelerating effect which neutral salts exert on the rate of hydrolysis of sucrose and of esters under the influence of acids is well known, but in spite of the great amount of work which has been done on the subject, no satisfactory explanation of the phenomena in question has been obtained. Quite recently the investigation of this problem has been taken up systematically at the Nobel Institute in Stockholm, under the direction of Arrhenius, to whom much of our knowledge of neutral salt action is due, and is being extended to the effect of neutral salts on other properties of solutions (compare Rivett, *Medd. k. Vetenskapsakad. Nobel-institut*, 1911, **2**, No. 9; Poma, *ibid.*, No. 11; Lundén, *ibid.*, No. 15).

An important advance in this subject has recently been made by Goldschmidt (*Zeitsch. Elektrochem.*, 1911, **17**, 684) and by Bredig (*ibid.*, 1912, **18**, 535) and Snethlage (*ibid.*, 1912, **18**, 539), who have shown that in the hydrolysis of esters in acid solution both the hydrions and the non-ionised acid are catalytically active. Snethlage in particular has extended these results to aqueous solutions, and calculates that in the case of a strong acid, such as hydrochloric acid, the non-ionised portion is in equivalent concentration more active than the ionised part. The accelerating influence of neutral salts with an ion in common with the acid is then simply explained as being due to their effect in diminishing the ionisation of the acid, and thus increasing the concentration of the more active part (compare also Acree, *Amer. Chem. J.*, 1912, **48**, 352).

Comparatively little work has hitherto been done on the effect of neutral salts on the catalytic activity of bases. Arrhenius (*Zeitsch. physikal. Chem.*, 1887, **1**, 110) and Spohr (*ibid.*, 1888, **2**, 194) showed many years ago that neutral salts in general diminish the rate of hydrolysis of esters by bases. The first systematic investigation of an accelerating effect of neutral salts in alkaline solution was described in an earlier paper (Senter, Trans., 1907, **91**, 460), in which it was shown that sodium salts of inorganic acids accelerate the rate of decomposition of sodium chloroacetate and bromoacetate in the presence of alkali to the extent of about 50 per cent. in molar solution. The only striking deviation from this result was the effect of sodium formate, which in molar solution produced an acceleration of about 200 per cent. in the case of sodium bromoacetate at 70° (compare Proc., 1908, **24**, 89; *Zeitsch. physikal. Chem.*, 1910, **70**, 54). Partly in order to account for the remarkable behaviour of sodium formate, the investigation has now been extended to the effect of sodium salts of organic acids (and other inorganic acids) on the rate of decomposition of sodium bromoacetate by alkali at 50°. For the sake of comparison the influence of the same salts on the hydrolysis of a non-electrolyte, namely, ethyl acetate, by alkali has also been investigated under the same conditions.

EXPERIMENTAL.

The salts used in the investigation were twice recrystallised, and the amount of water of crystallisation (if any) was carefully determined in the usual way. 2*N*-Solutions were then prepared (twice molar for salts of monobasic acids, molar for salts of dibasic acids), and when equal volumes of these solutions and the bromoacetate–alkali mixture were used, the solutions were normal with respect to neutral salt. Great care was taken to ensure that the solutions were neutral with respect to phenolphthalein. The experiments were carried out as described in the previous paper (*loc. cit.*, p. 465). In each series duplicate titrations were carried out, and four independent series of measurements were made in order to ensure accuracy. The results are summarised in the accompanying table.

TABLE I.

Sodium Bromoacetate, N/10, *and Sodium Hydroxide*, N/10.
Temperature 50·0°.

Neutral salt.	Velocity-coefficient.	Increase, per cent.
None	0·00052	—
Sodium chlorate, *N*/1	0·00082	51
,, ferrocyanide, *N*/1 (*M*/4)	0·00090	53
,, benzenesulphonate, *N*/1	0·00082	51
,, benzoate, *N*/1	0·00082	51
,, formate, *N*/1	0·00104	100
,, tartrate, *N*/1	0·00102	98
,, acetate, *N*/1	0·00106	102
,, salicylate, *N*/1	0·00052	none
,, succinate, *N*/1	0·00116	122

It should be mentioned that whilst the reaction is strictly bimolecular in the presence of salts of inorganic acids, the velocity-coefficient tends to increase slightly in the presence of salts of organic acids. This is illustrated by the results in the presence of sodium acetate and of sodium tartrate, quoted in the accompanying table.

Table II.

Sodium Bromoacetate and Sodium Hydroxide, N/10, *at* 50·4°.

Sodium Acetate, N/1.			*Sodium Tartrate*, N/1.		
t (min.).	$a-x$.	k.	t (min.).	$a-x$.	k.
0	19·8	—	0	19·8	—
60	12·1	0·0103	60	12·4	0·0097
180	6·85	0·0103	180	7·15	0·0097
360	3·75	0·0113	360	4·1	0·0105

Table III contains the results of the corresponding experiments on the decomposition of ethyl acetate in alkaline solution at 19·6°. For those salts which were investigated from this point of view by Arrhenius the acceleration per cent. is quoted in the fourth column.

Table III.

Ethyl Acetate, N/40, *Sodium Hydroxide*, N/40.

Temperature 19·6°.

Neutral salt.	Velocity-coefficient.	Increase, per cent.	
		Senter and Bulle.	Arrhenius.
None	0·0090	—	—
Sodium nitrate, *N*/1	0·0073	−19	−22·4
,, chlorate, *N*/1	0·0079	−12	—
,, sulphate, *N*/1	0·0105	+12	+12
,, ferrocyanide *N*/1	0·0090	0	—
,, formate, *N*/1	0·0093	+ 3	—
,, acetate, *N*/1	0·0090	0	− 0·3
,, tartrate, *N*/1	0·0097	+ 8	—
,, succinate, *N*/1	0·0097	+ 8	—
,, benzoate, *N*/1	0·0045	−100	—
,, salicylate, *N*/10	0·0045	—	—
,, ,, *N*/20	0·0063	—	—

The agreement with the results of Arrhenius when observations were made with the same salts as those used in the present investigation is excellent.

The figures quoted in table III show that the effect of neutral salts of organic acids on the hydrolysis of ethyl acetate, like that of the salts of inorganic acids, is, as a rule, small, and may be positive or negative. The markedly retarding effect exerted by monosodium salicylate is further referred to below (p. 2533). On the other hand, sodium salts of organic acids exert a still greater accelerating influence on the decomposition of sodium bromoacetate than do the corresponding salts of inorganic acids (table I).

The results of experiments which have to a great extent accounted for this discrepancy between the activities of organic and inorganic salts will now be described. The equation representing the hydrolysis of sodium bromoacetate by alkali is usually written as follows:

$$CH_2Br\cdot CO_2Na + NaOH = OH\cdot CH_2\cdot CO_2H + NaBr,$$

and according to this equation the rate of formation of glycollic acid should be the same as the rate of formation of bromine ions (that is, of sodium bromide). The same should be true of the decomposition in neutral solution, represented by the equation:

$$CH_2Br\cdot CO_2Na + H_2O = OH\cdot CH_2\cdot CO_2H + HBr.$$

We have now found that when a neutral solution of sodium bromoacetate is heated with sodium acetate the acidity of the solution, as determined by titration with alkali, increases at first much more slowly than the bromine ion concentration, as determined in a parallel experiment by titration with silver nitrate. This is illustrated by the following numbers.

TABLE IV.

Sodium Bromoacetate, N/10, *Sodium Acetate*, N/1.

Temperature 49·8°. (10 c.c. titrated in each experiment.)

Time (hours)	0	3	5	22
C.c. of $N/50$-AgNO$_3$	0	9·7	15·2	39·1
,, $N/50$-NaOH	0	0·7	1·9	—

The simplest explanation of these results would appear to be that sodium acetate reacts with the bromoacetate according to the equation:

$$CH_2Br\cdot CO_2Na + CH_3\cdot CO_2Na = CH_3\cdot CO\cdot O\cdot CH_2\cdot CO_2Na + NaBr$$

with formation of sodium acetoxyacetate, which in aqueous solution is only hydrolysed very slowly into sodium glycollate and acetic acid. In consequence of this, the bromine-ion concentration must increase much more rapidly than the acid concentration, as is actually found. The experimental proof of this view of the mechanism of the reaction and its bearing on the hydrolytic decomposition of sodium bromoacetates in neutral solution is given in the succeeding paper (p. 2534).

The next point to be investigated is whether the liberation of bromine ions and the formation of acid increase at the same rate in alkaline solution; in other words, whether the intermediate compound, sodium acetoxyacetate, is decomposed by alkali into sodium acetate and sodium glycollate as fast as it is produced. A typical experiment designed to solve this question is quoted in table V. The rate at which the alkali is neutralised in the course of the action was followed by titrating the solutions with standard sulphuric acid, and the rate of change of the bromine-ion concentration was determined with $N/50$-silver nitrate by the thiocyanate method.

TABLE V.

Sodium Bromoacetate and Sodium Hydroxide, N/10; *Sodium Acetate*, N/1. Temperature 50·0°; 10 c.c. titrated.

Time (minutes)	0	30	90	180
C.c. $N/20$-H_2SO_4 used	19·75	15·05	10·10	6·50
Acid formed (c.c. $N/50$-alkali).........	0	11·75	24·1	33·1
Br' concentration (c.c. $N/50$-$AgNO_3$)	0	11·55	24·05	33·4

The figures in the last two lines, in which the acid and bromine-ion concentrations are expressed in equivalent units, show that they increase at the same rate, from which it follows that sodium acetoxyacetate is hydrolysed in alkaline solution as fast as it is formed, according to the equation:

$$CH_3\cdot CO\cdot O\cdot CH_2\cdot CO_2Na + NaOH = CH_3\cdot CO_2Na + OH\cdot CH_2\cdot CO_2Na.$$

This conclusion has been confirmed by direct experiments with the compound itself, which was prepared for the purpose; the details are given in the paper just mentioned.

The effect of sodium tartrate on the hydrolytic decomposition of sodium bromoacetate in neutral solution was also investigated; the results were similar to those with sodium acetate already described. When, however, sodium chlorate is used instead of the salts of organic acids, the bromine-ion concentration and the acidity increased at exactly the same rate, which is slightly less than the speed in the absence of chlorate.*

The greater neutral salt effect of organic salts on the rate of hydrolysis of sodium bromoacetate by alkali is thus satisfactorily accounted for. It is due to the intermediate formation of acyloxyacetates of the type $OR\cdot CH_2\cdot CO_2Na$ (R = acid group), which are hydrolysed much more rapidly by alkali than sodium bromoacetate itself.

The experiments show that the ClO_3' group, unlike the negative components of weak organic acids, cannot take the place of the bromine atom in sodium bromoacetate, since the rate of hydrolysis of the latter salt is not accelerated, but, as just pointed out, very slightly retarded by the presence of sodium chlorate in neutral solution.

The Second Dissociation Constant of Salicylic Acid.—It remains

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* The velocity-coefficient in aqueous solution is 0·0000090; when the solution is $N/1$ with respect to sodium chlorate, the coefficient is 0·0000085.

to explain the fact that sodium salicylate not only does not show the great accelerating effect of salts of other organic acids, but has a powerful retarding action on the hydrolysis of ethyl acetate. The obvious explanation is that a certain amount of disodium salicylate is formed according to the reversible reaction:

$$OH\cdot C_6H_4\cdot CO_2Na + NaOH \rightleftarrows ONa\cdot C_6H_4\cdot CO_2Na + H_2O.$$

The concentration of the free alkali being thus reduced, the speed of the reaction is naturally diminished.

The difference between the observed and calculated velocity in the presence of sodium salicylate furnishes data from which the dissociation-constant of the phenolic hydroxyl may be calculated. For this purpose it is most advantageous to use the data with ethyl acetate, as in this case the neutral salt action must be very small. At 19·6° it was found that whilst the velocity-coefficient for $N/40$-ethyl acetate and $N/40$-sodium hydroxide is 0·0090, in $N/20$-sodium salicylate the constant is 0·0060 and in $N/10$-salicylate 0·0045. In $N/20$-solution, therefore, only two-thirds of the sodium hydroxide is free; the remainder has combined to form disodium salicylate, the concentration of which is therefore one-third of $N/40$ or 0·0083. Substituting in the general equations for the hydrolysis of the salt of a strong base and a weak acid, we have:

$$[\text{Base}]\,[\text{acid}]/\text{salt} = [NaOH]\,[OH\cdot C_6H_4\cdot CO_2Na]/[ONa\cdot C_6H_4\cdot CO_2Na]$$
$$= [0{\cdot}0166]\,[0{\cdot}0416]/[0{\cdot}0083] = 0{\cdot}083 = k_h \text{ (hydrolysis-constant).}$$

The value of the hydrolysis-constant calculated from the experiment in $N/10$-solution is 0·0875; the mean is therefore 0·085. Substituting in the formula $k_h = k_w/k_a$, where k_w is the dissociation-constant of water at 19·6° and k_a that of monosodium salicylate, we obtain for the latter $k_a = k_w/k_h = 0{\cdot}8 \times 10^{-14}/0{\cdot}085 = 1 \times 10^{-13}$ approximately. Somewhat similar measurements have already been made by Goldschmidt in another connexion (*Ber.*, 1907, **40**, 637), but the dissociation-constant of the hydroxyl group of salicylic acid was not calculated from the observations. The above result is merely preliminary; further measurements will be made with greater variation in the concentrations of the reacting substances, and the observations will be extended to salts of other hydroxy-acids.

Nature of Neutral Salt Action.

The provisional explanation of neutral salt action given in an earlier paper (Senter, *Zeitsch. physikal. Chem.*, 1910, **70**, 518) that the phenomenon "is due, in part at least, to the influence of one or other of the ions in modifying, according to the laws of chemical equilibrium, the concentration of the intermediate products which determine the velocity of the particular reaction," is supported by the results of Snethlage, already referred to, and especially by the results described in the present paper. As regards the hydrolysis of ethyl acetate, on the rate of which neutral salts have only a very secondary influence, the conclusion may be drawn that the substances the reactivity of which determines the speed of the reaction contain no ion in common with the neutral salts used.

The alternative explanation of neutral salt action on the basis of the hydrate theory (compare Caldwell, *Proc. Roy. Soc.*, 1906, A, **78**, 272; Armstrong, *ibid.*, 1908, A, **81**, 80) appears to be incompatible with the results described in the present paper, more particularly as regards the fundamental difference in the effect of such salts on the hydrolysis of sodium bromoacetate and ethyl acetate respectively in alkaline solution (compare also Trans., 1907, **91**, 460). A similar conclusion has also been reached by the workers in the Nobel Institute (Rivett, *loc. cit.*; Lundén, *loc. cit.*).

Summary.

(1) Sodium salts of organic acids, like the corresponding salts of inorganic acids, have only a slight effect on the rate of hydrolysis of ethyl acetate in alkaline solution.

(2) Sodium salts of organic acids accelerate the hydrolysis of sodium bromoacetate by alkali to a still greater extent than do the salts of inorganic acids.

(3) This effect has been traced, taking sodium acetate as a type, to the intermediate formation of sodium acyloxyacetates (for example, sodium acetoxyacetate), which are hydrolysed by alkali as fast as they are formed.

(4) From the extent to which the hydrolysis of ethyl acetate by alkali is retarded by monosodium salicylate, a provisional estimate of the second acid dissociation-constant of salicylic acid at 20° has been made.

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CCLXIII.—*Reactivity of the Halogens in Organic Compounds. Part VII. The Formation of Intermediate Compounds in the Hydrolysis of Sodium Bromoacetate.*

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In the preceding paper, dealing with the phenomenon of neutral salt action, it was mentioned that when sodium bromoacetate is heated with sodium acetate either in neutral or alkaline solution the substances interact to form sodium acetoxyacetate, according to the equation:

$$CH_2Br\cdot CO_2Na + CH_3\cdot CO_2Na = CH_3\cdot CO\cdot O\cdot CH_2\cdot CO_2Na + NaBr \qquad (1)$$

This intermediate compound is hydrolysed slowly in aqueous solution, rapidly in alkaline solution, to acetic and glycollic acids (or their sodium salts). In the present paper, the evidence in favour of these statements is given, and the effect of formates and certain other salts has been investigated on the same lines. Further, from analogy we may anticipate the intermediate formation of bromoacetoxyacetate when sodium bromoacetate is heated alone in sufficiently concentrated solution, according to the equation:

$$CH_2Br\cdot CO_2Na + CH_2Br\cdot CO_2Na = CH_2Br\cdot CO\cdot O\cdot CH_2\cdot CO_2Na + NaBr \qquad (2)$$

The mechanism of the hydrolysis of sodium bromoacetate and halogen-substituted derivatives of this type is of fundamental importance in connexion with the Walden inversion, and the reaction has therefore been investigated from this point of view.

Effect of Sodium Acetate and Sodium Formate on the Hydrolysis of Sodium Bromoacetate in Neutral Solution.

The starting point of this phase of the investigation was the discovery that when sodium bromoacetate is heated with sodium acetate in neutral solution the rate of increase of the bromine-ion concentration is not equal to the rate of increase of acidity, as should be the case if the reaction proceeds according to the generally accepted equation:

$$CH_2Br\cdot CO_2Na + H_2O = OH\cdot CH_2\cdot CO_2Na + NaBr;$$

but the former increases much more rapidly than the latter, as shown in the accompanying table.

TABLE I.

Sodium Bromoacetate, *N*/5. Sodium Acetate, *N*/1.
Temperature, 49·9°.

t (min.).	Br′ concentration (c.c. *N*/50-$AgNO_3$).	Unchanged bromoacetate.	Concentration of free acid (c.c. *N*/50-NaOH).	k.
0	0·0	100·0	0·0	—
30	4·3	95·7	—	0·0000288
90	11·6	88·4	—	0·0000283
180	21·7	78·3	—	0·0000280
300	32·9	67·1	2·0	0·0000278
∞	100·0	0·0	—	—

The numbers in the second column were obtained by adding 10 c.c. of the reaction mixture to a slight excess of *N*/50-silver nitrate solution, and titrating back with $N/50$-thiocyanate; the concentration of free acid by titrating another 10 c.c. directly with standard sodium hydroxide solution.

The results show, in the first place, that the bromine-ion concentration increases much more rapidly than the acid concentration; at the end of three hundred minutes the former is more than sixteen times that of the latter under equivalent conditions. If the relatively rapid liberation of bromine ion is due to the intermediate formation of sodium acetoxyacetate, according to equation (1) the reaction should be bimolecular. In order to test this conclusion, the data were substituted in the ordinary equation for a bimolecular reaction: $0{\cdot}4343k = 1/[t(a-b)] \log_{10}[b(a-x)]/[a(b-x)]$, and the approximate agreement of the values of k in the fifth column of the table supports the above suggestion as to the mechanism of the reaction.

The bimolecular reaction represented in equation (1) must be followed by a unimolecular reaction representing the hydrolysis of sodium acetoxyacetate, but as the latter change is so slow (compare table I, column 4, and also p. 2540), a more detailed series of measurements has been made with sodium formate, in which case the intermediate compound is much more rapidly hydrolysed. The results are given in table II.

TABLE II.

Sodium Bromoacetate, $N/5$. Sodium Formate, $N/1$.
Temperature, 49·9°.

t (min.).	Br′ concentration (c.c. $N/50$-$AgNO_3$).	Un-changed bromo-acetate.	Acid concentration (c.c. $N/50$-NaOH).		Formoxy-acetate concentra-tion.	k_1.
			Found.	Calculated.		
0	0·0	100·0	0·0	—	0·0	—
30	4·7	95·3	0·87	0·5	3·8	0·00160
90	13·0	87·0	3·75	3·0	9·25	0·00155
180	24·1	75·9	10·1	9·7	14·0	0·00153
300	36·2	63·8	18·3	20·9	19·9	0·00150
360	41·3	58·7	24·4	26·6	16·9	0·00148
1320	86·15	13·85	74·0	—	12·15	—
∞	100·0	0·0	100·0	—	0·0	—

In order to make clear the significance of these figures, the probable mechanism of the reaction must be considered; it is represented in the following equations:

$$CH_2Br{\cdot}CO_2Na + H{\cdot}CO_2Na = HCO{\cdot}O{\cdot}CH_2{\cdot}CO_2Na + NaBr \qquad (a)$$

$$HCO{\cdot}O{\cdot}CH_2{\cdot}CO_2Na + H_2O = H{\cdot}CO_2Na + OH{\cdot}CH_2{\cdot}CO_2H \qquad (b)$$

$$CH_2Br{\cdot}CO_2Na + H_2O = OH{\cdot}CH_2{\cdot}CO_2H + NaBr \qquad (c)$$

The stages (a) and (b) are consecutive, and proceed simultaneously with stage (c). As, however, the latter reaction is very slow compared with (*a*) and (*b*), it may be neglected for the present. The significance of the different columns in table II will now be evident. The second column represents the rate of reaction (*a*); the fourth column that of reaction (*b*), and the sixth column the difference in the rates of reactions (*b*) and (*c*); in other words, the rate at which the intermediate compound, sodium formoxyacetate, accumulates in the solution. It will now be shown that the data in question are in quantitative accord with the above view as to the mechanism of the reaction.

Since sodium formate is present in large excess at the commencement of the reaction, and is regenerated in reaction (*b*), its concentration may be taken as approximately constant, and therefore reaction (*a*) should be unimolecular. The values for k_1 in column 6 show that this is the case; the slight falling in the magnitude of the coefficients is no doubt due to the neglect to take account of the slight variation in the formate concentration. The figures for 1320 minutes are of no value, as by that time reaction (*c*) cannot be neglected.

That two consecutive reactions occur is evident from the fact that the rate of formation of acid, the final stage in the reaction, is slow at first, and gradually increases to a maximum (column 4). A still more conclusive proof is to represent the results quantitatively by means of the formulæ for two consecutive unimolecular reactions. The most clear and thorough mathematical treatment of such reactions is due to Rakowski (*Zeitsch. physikal. Chem.*, 1907, **57**, 328), who has shown that for two consecutive irreversible reactions, $m_1 \longrightarrow m_2 \longrightarrow m_3$, the concentration of the final product, m_3, at the time t is represented by the equation:

$$[M_3] = a_1\left\{1 - \frac{1}{k_2 - k_1}\left[k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right]\right\},$$

where a_1 is the initial concentration of m_1 (in this case sodium bromoacetate), and k_1 and k_2 are the velocity-coefficients of the reactions $m_1 \longrightarrow m_2$ and $m_2 \longrightarrow m_3$ respectively. In the present instance k_1 is 0·0016 approximately, and it has been found by trial that the above equation is satisfied when k_2, the rate of hydrolysis of sodium formoxyacetate, is taken as 0·0056. This is shown in table II, columns 4 and 5, in which the observed and calculated values of m_3 at the time t are compared. The agreement, when the rapid variation in the alkali concentration with time is taken into account, is fairly good, and conclusive proof is thus afforded that the mechanism of the reaction is as stated above.

Hydrolysis of Acetoxyacetic Acid.

In order to elucidate the behaviour of one of the intermediate compounds which are formed when sodium bromoacetate is heated with alkali salts of organic salts in aqueous solution, acetoxyacetic acid has been prepared, and the rate of hydrolysis of the free acid and of its sodium salt in neutral and alkaline solution has been measured. The acid was prepared by the action of acetyl chloride on glycollic acid according to Anschütz and Bertram's method (*Ber.*, 1903, **36**, 467), twice recrystallised from chloroform, and its purity controlled by titration with alkali, and by its melting point, 66°. Aqueous solutions of the acid of definite strength were then prepared and heated at constant temperature, portions being removed from time to time and titrated with standard sodium hydroxide and phenolphthalein as indicator. The results of typical measurements at 49·5° and 25·2° are given in table III.

TABLE III.

Acetoxyacetic Acid, $N/5$.

Temperature 49·5°.			Temperature 25·2°.		
t (hrs.).	$a-x$.	k.	t (hrs.).	$a-x$.	k.
0	40·0	—	0	40·0	—
3	38·0	0·0170	23	37·8	0·0025
6	36·1	0·0170	47	35·6	0·0025
24	26·8	0·0166	71	33·9	0·0024
48	18·6	0·0162	143	28·2	0·0025

The values of k in the third and sixth columns are calculated by means of the equation for a unimolecular reaction, and, as the figures show, well-agreeing constants are obtained. When, however, varying initial concentrations of the acid are used, it is found that the velocity-coefficients are smaller the lower the concentration; thus the constant for a $N/10$-solution at 25·2° is 0·0018. The most rational explanation is that the acid itself, or rather the hydrions, exerts a catalytic effect on the reaction. To test this suggestion, an experiment was made in which hydrochloric acid was added at the commencement; the results are given in table IV.

TABLE IV.

Acetoxyacetic Acid, $N/5$. Hydrochloric Acid, $N/5$.
Temperature, 49·9°.

t (hrs)	0	1	2	3·5	5·5
Acetoxyacetic acid concn.	39·6	28·9	21·55	14·3	7·7
k	—	0·31	0·30	0·30	0·30

As the figures show, the action is greatly accelerated by the addition of hydrochloric acid, and remains unimolecular. Rath (*Annalen*, 1908, **358**, 98) showed some years ago that this reaction is unimolecular, and that the velocity-coefficients are greater in the more concentrated solutions. He concluded rightly that hydrions accelerate the reaction, but did not test his suggestion by examining the effect of a strong acid.

Neutral salts have a slight accelerating influence on the reaction velocity; thus the coefficient for a $N/5$-solution is 0·00212, both in $N/1$-sodium chlorate and $N/1$-sodium nitrate, whilst in the absence of the neutral salts it is 0·00170.

The average temperature-coefficient of the reaction for 10° between 25·2° and 49·5°, as calculated from the data in table III, is 2·1.

Hydrolysis of Sodium Acetoxyacetate.

Sodium acetoxyacetate undergoes hydrolysis in neutral solution much more slowly than the free acid under equivalent conditions. This is illustrated by the data of an experiment at 49·9°.

TABLE V.

Sodium Acetoxyacetate, $N/5$. Temperature 49·9°.

t (hrs.)…………	0	2	6	24	48
$a-x$……………	40·0	39·85	39·65	38·7	38·0
k ………………	—	—	0·0014	0·0014	0·0012

A comparison with the data in table III gives the interesting result that the free acid under equivalent conditions is hydrolysed more than ten times as fast as the neutral salt. The explanation is doubtless to be found in the absence of hydrions in the latter solution—as pointed out above, they exert an accelerating effect on the reaction.

It remains to deal with the hydrolysis of sodium acetoxyacetate in alkaline solution. In contrast to the very slow rate of reaction in neutral solution, the velocity of hydrolysis by alkali is so rapid that the measurements had to be carried out at 0°. At definite intervals a measured volume of the mixture was removed, added to excess of dilute sulphuric acid, which practically stopped the reaction, and the solution titrated with dilute alkali. The results of a typical experiment are given in table VI.

TABLE VI.

Sodium Acetoxyacetate, *N*/10. Sodium Hydroxide, *N*/10.
Temperature 0·4°.

t (min.)	0	5	15	30	60	120
$a-x$	24·05	21·15	17·25	13·5	9·5	6·15
k	—	0·0011	0·0010	0·0010	0·0010	0·0010

As the table shows, well-agreeing constants for a bimolecular reaction are obtained. The difference in the rate of hydrolysis of sodium acetoxyacetate in water and in alkali is remarkable, the speed in *N*/10-sodium hydroxide being at least 100,000 times that in water. In this respect acetoxyacetic acid resembles the ordinary esters, and differs from the monohalogen-substituted fatty acids, for which the rate of hydrolysis in neutral and alkaline solution is of the same order.

Neutral salts have only a slight accelerating effect on the alkaline hydrolysis of sodium acetoxyacetate; both in *N*/1-sodium nitrate solution and in *N*/1-sodium chlorate solution the velocity-coefficient is 0·0012, as compared with 0·0010 in aqueous solution.

Hydrolysis of Sodium Bromoacetate in Neutral Solution.

As sodium acetate reacts with sodium bromoacetate on heating, with formation of sodium acetoxyacetate (p. 2536), it is natural to suppose that when sodium bromoacetate is heated alone in sufficiently concentrated solution, sodium bromoacetoxyacetate must be formed according to the equation:

$$CH_2Br\cdot CO_2Na + CH_2Br\cdot CO_2Na = CH_2Br\cdot CO\cdot O\cdot CH_2\cdot CO_2Na + NaBr \quad (a)$$

Provided that sodium bromoacetoxyacetate is formed faster than it is hydrolysed, according to the equation:

$$CH_2Br\cdot CO\cdot O\cdot CH_2\cdot CO_2Na + H_2O = CH_2Br\cdot CO_2Na + OH\cdot CH_2\cdot CO_2H \quad (b)$$

the intermediate formation of this compound can be tested by simultaneous titration of the bromine ions and of the free acid produced. The results of two series of measurements with *N*/10- and 2*N*-sodium bromoacetate solution are given in table VII.

TABLE VII.

Sodium Bromoacetate Solution. Temperature, 49·8°.

$N/10$-solution.				$2N$-solution.		
(hrs.).	Br′-concentration (c.c. $N/50$-$AgNO_3$).	Concentration of free acid (c.c. $N/50$-NaOH).	k.	t (hrs.).	Br′-concentration (c.c. $N/50$-$AgNO_3$).	Concentration of free acid (c.c. $N/50$-NaOH).
0	0·0	0·0	—	0	2·2	0·0
1	0·30	0·25	—	0·5	8·7	0·5
3	1·15	0·75	—	1	14·5	1·75
7	2·4	2·0	0·0031	2	25·9	4·9
25	7·4	6·1	0·0028	5	58·7	19·0
49	13·9	11·5	0·0029	10·5	93·6	45·5
72	18·5	16·6	0·0028	[∞	200·0	200·0]
[∞	50·0	50·0]				

A consideration of the data in the table reveals a number of points of considerable interest. In the first place, the rate of increase of the bromine-ion concentration and that of the acid in the $N/10$-solution is about the same, from which the conclusion may be drawn that the bimolecular reaction (a) is of secondary importance, and that the reaction proceeds mainly by direct hydrolysis of sodium bromoacetate according to the equation:

$$CH_2Br\cdot CO_2Na + H_2O = OH\cdot CH_2\cdot CO_2H + NaBr \quad . \quad . \quad (c)$$

If this is the case, the rate of formation of bromine ions should be represented by the formula for a unimolecular reaction, and the good agreement of the velocity-coefficients in column 4 show that such is the case.

Turning now to the concentrated solution, the great difference in the rate of formation of bromine ions and free acid, and the form of the curve representing the rate of increase of acid with time show conclusively on comparison with the results given in table II that in this case also we have to deal with two consecutive reactions; doubtless those represented by equations (a) and (b) (p. 2540). If this suggestion is correct, the rate of increase of the bromine-ion concentration should follow the course of a bimolecular reaction, provided that the direct formation of glycollic acid according to equation (c) can be neglected in the early stages of the reaction. Unfortunately, in so concentrated solution reaction (c) cannot be neglected, and an attempt to allow for this reaction in a formula has revealed mathematical difficulties which have not yet been entirely overcome. The matter will be discussed again in a later paper.

Additional confirmation of the above view as to the mechanism of the reaction could be obtained by examination of the behaviour of the hypothetical intermediate compound, sodium bromoacetoxyacetate. Attempts to isolate his compound from solution or to prepare it by the action of bromoacetylbromide or glycollic acid, have hitherto proved unsuccessful, but other methods of preparing it may give better results. In any case, the results so far obtained appear to show conclusively that the above view as to the mechanism of the reaction is the correct one.

Quite recently, B. Holmberg (*Ber.*, 1912, **45**, 1713) has found that when the sodium salt of monobromosuccinic acid is heated in aqueous solution the bromine-ion concentration increases faster than that of the free acid, and accounts for this result on the assumption of the intermediate formation of a lactone which combines relatively slowly with water to form the corresponding acid. It has already been pointed out (Senter, *Ber.*, 1912, **45**, 2318) that such an assumption cannot account for the similar results obtained by us with sodium bromoacetate at a much earlier date (compare Proc., 1911, **27**, 511), and as Holmberg has not proved the presence of a lactone or even investigated the effect of dilution on the relative proportions of bromine ions and acid formed, his suggestions as to the mechanism of the hydrolysis of sodium bromosuccinate are of doubtful validity and are certainly premature. Further investigation must decide the question as to whether the theory developed in the present paper is of general application to the hydrolysis of monohalogen-substituted acids.

The bearing of these results on the Walden inversion will be dealt with in a later paper (compare Frankland, Proc., 1911, **27**, 152; Senter, *ibid.*, 153).

In conclusion, we desire to express our obligations to the Research Fund Committee of the Chemical Society for a grant which has defrayed the greater part of the cost of this investigation and that described in the preceding paper.

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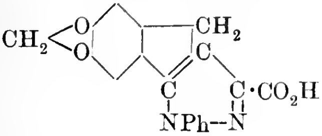
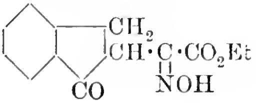
CCLXIV.—*Studies on Cyclic Ketones. Part II.*

By SIEGFRIED RUHEMANN and STANLEY ISAAC LEVY.

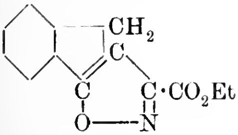
IN Part I. of the present work (Ruhemann, this vol., p. 1729) the condensation of ethyl oxalate with various cyclic ketones has been described, and in particular an account has been given of the polycyclic systems obtained by condensation of the ester produced by this reaction from 1-hydrindone, namely, ethyl-1-hydrindone-2-

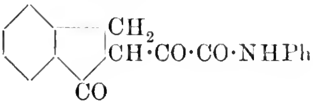
oxalate. It was shown that with phenylhydrazine this compound forms ethyl phenylindenopyrazolecarboxylate. In the same way, it is now found that the corresponding methylenedioxy-1-hydrindone-2-oxalic acid yields the analogous indenopyrazole derivative (I):


(I.)


(II.)

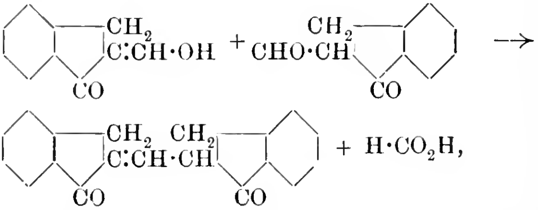
With a view to the preparation of similar polycyclic compounds, ethyl 1-hydrindone-2-oxalate has now been treated with other reagents. By the action of hydroxylamine, the oxime (II) is produced; this, however, could not be condensed to ethyl indeno-*iso*oxazolecarboxylate (III), nor was it possible to effect condensation of the anilide (IV), which is readily formed by the action of aniline on the ester.


(III.)

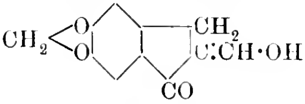

(IV.)

Our attention has been more especially directed to the study of the action of ethyl formate on cyclic ketones, and to the properties of the hydroxymethylene derivatives which are so formed. The results already obtained are of sufficient interest to induce us to investigate these compounds more closely. The hydroxymethylene derivatives of the fatty and fatty aromatic series, and of the cyclic ketone, camphor, were discovered and examined by Claisen and his pupils. Most of these compounds were found to be stable at fairly high temperatures, and could be distilled in a vacuum without undergoing any change; thus, in the case of hydroxymethylenecamphor, although the impure substance is transformed on keeping into a viscid, yellow mass, it was shown that the pure compound could be obtained from this, on distillation with steam, or in a vacuum.

The behaviour of 2-hydroxymethylene-1-hydrindone, and of its methylenedioxy-derivative, which we have now prepared, is in marked contrast to that of hydroxymethylenecamphor and other hydroxymethylene derivatives examined by Claisen. These compounds are not stable towards heat, but suffer a remarkable condensation, involving the loss of one molecule of formic acid from two molecules of the substance. In the case of 2-hydroxymethylene-1-hydrindone, the change takes place very readily, occurring even on attempting to dry the substance in the steam-oven; the colourless hydroxymethylene compound, which is readily soluble in alcohol, is transformed into the deep red condensation product, which is practically insoluble in alcohol. The transformation occurs with even greater ease at 112°; the compound fuses with ebullition to a red liquid, which soon sets to a solid, and on further heating this melts and decomposes at 232°. The condensation is to be represented thus:



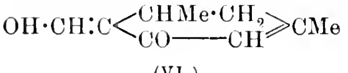
and the product is therefore to be regarded as ketohydrindylmethyleneketohydrindene. This constitution is supported by the fact that the substance dissolves readily in alkalis on warming, to yield purple solutions, which doubtless contain salts of the compound. With hydroxymethylenemethylenedioxy-1-hydrindone (V)



(V.)

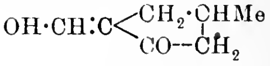
the change occurs less readily, and requires a higher temperature, but otherwise the two cases are similar.

On account of this behaviour, hydroxymethylene derivatives of other cyclic ketones have been prepared and examined; but both 6-hydroxymethylene-1:3-dimethyl-Δ^3-*cyclo*hexen-5-one (VI), a yellow oil, and 5-hydroxymethylene-3-methyl*cyclo*pentan-1-one (VII), a



$\mathrm{OH\cdot CH{:}C}<\begin{matrix}\mathrm{CHMe\cdot CH_2}\\ \mathrm{CO{-}{-}{-}{-}CH}\end{matrix}>\mathrm{CMe}$

(VI.)

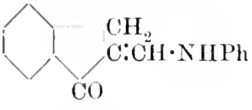


$\mathrm{OH\cdot CH{:}C}<\begin{matrix}\mathrm{CH_2\cdot CHMe}\\ \mathrm{CO{-}{-}CH_2}\end{matrix}$

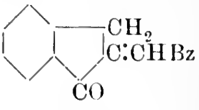
(VII.)

very volatile, white solid, can be distilled in a vacuum without undergoing any change, and as yet we have not been able to observe that either of them can undergo a similar transformation.

In other respects, the hydroxymethylene compounds of the



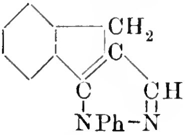
(VIII.)



(IX.)

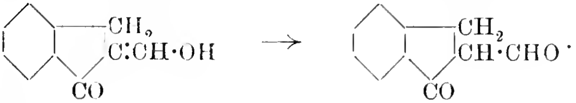
hydrindene series behave quite normally. Hydroxymethylene-8-hydrindone readily forms a copper salt; it reacts with aniline to yield an anilide (VIII), insoluble in potassium hydroxide, and with benzoyl chloride, forming the benzoyl derivative (IX). It gives a semicarbazone (X), soluble in alkali, and with phenylhydrazine it condenses to the phenylindenopyrazole (XI); thus it appears that

(X.)



(XI.)

under the influence of these two reagents, the hydroxymethylene-ketone is transformed into the tautomeric aldehydoketone, thus:



Experimental.

5 : 6-*Methylenedioxy*-1-*phenyl*-4 : 5-*indenopyrazole*-3-*carboxylic Acid* (I).

It has been already stated (this vol., p. 1735) that ethyl 5 : 6-methylenedioxy-1-hydrindone-2-oxalate, which is formed by the action of ethyl oxalate on 5 : 6-methylenedioxy-1-hydrindone, could not be prepared pure, although the acid can readily be obtained in the pure state by hydrolysis of the ester. On treatment of the hot aqueous solution of the acid with phenylhydrazine hydrochloride, a white, crystalline solid separates, which is soluble in boiling glacial acetic acid, and crystallises on cooling in colourless needles, darkening at 235°, and charring completely at 255°:

0·2080 gave 0·5157 CO_2 and 0·0685 H_2O. C=67·61; H=3·66.

$C_{18}H_{12}O_4N_2$ requires C=67·50; H=3·75 per cent.

1-*Hydrindone*-2-*oxanilide* (IV).

This substance is readily obtained on adding an excess of aniline to an ethereal solution of ethyl 1-hydrindone-2-oxalate; in the course of a few days a yellow, crystalline solid separates, which is sparingly soluble in boiling alcohol, but readily so in boiling xylene, crystallising on cooling in yellow needles, which soften at 223° and melt at 228°:

0·2045 gave 0·5480 CO_2 and 0·0865 H_2O. C=73·08; H=4·70.

0·2300 ,, 10·4 c.c. N_2 at 20° and 757 mm. N=5·15.

$C_{17}H_{13}O_3N$ requires C=73·12; H=4·66; N=5·02 per cent.

The alcoholic solution of the compound gives a dark brown coloration on the addition of ferric chloride.

Attempts were made to condense the anilide, but without success. Acetic anhydride and acetyl chloride have no action on it. In cold concentrated sulphuric acid it dissolves to form a yellow solution; this, after keeping overnight, and then pouring on ice, yields a yellow, gelatinous product, which is readily soluble in alkalis, and is reprecipitated from the alkaline solution on the addition of dilute hydrochloric acid. This product is also soluble in boiling water, separating again on cooling in a gelatinous condition; owing to this fact, and to its insolubility in all ordinary organic solvents, we have been unable to determine its composition; but qualitative tests indicate that it is a sulphonic acid of the anilide.

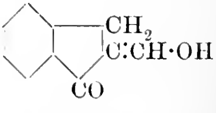
The Oxime of Ethyl 1-*Hydrindone*-2-*oxalate* (II).

In order to prepare this compound, ethyl 1-hydrindone-2-oxalate (3 grams), dissolved in alcohol, is treated with an aqueous solution of hydroxylamine hydrochloride (3 grams) and an excess of solid sodium hydrogen carbonate. The mixture is kept overnight, and on addition of dilute sulphuric acid, a white solid is precipitated; this is moderately soluble in ether, and is obtained from the solution on the addition of light petroleum in colourless prisms, softening at 148° and melting at 156° to a red liquid. The oxime dissolves readily in sodium carbonate; it is also soluble in alcohol, the solution giving a faint coloration with ferric chloride:

0·2045 gave 0·4730 CO_2 and 0·0970 H_2O. C=63·08; H=5·27.
0·2200 ,, 11·2 c.c. N_2 at 22° and 756 mm. N=5·73.
$C_{13}H_{13}O_4N$ requires C=63·17; H=5·27; N=5·67 per cent.

With the object of transforming the oxime into the *iso*oxazole (III) it was heated to a temperature of 160—170°, when a red oil was obtained, which solidified on cooling; but the solid, after recrystallisation from dilute alcohol, was found to be the unchanged oxime. Nor could condensation to the *iso*oxazole be effected by heating with acetic anhydride and glacial acetic acid, a resinous product being formed; although Tingle (*Amer. Chem. J.*, 1897, **19**, 409), using the same method, states that he succeeded in condensing the oxime of ethyl camphoroxalate to the corresponding *iso*oxazole.

2-*Hydroxymethylene*-1-*hydrindone*,



This substance is readily obtained by adding to dry sodium ethoxide, suspended in absolute ether, an ethereal solution of

1-hydrindone (6·6 grams) and ethyl formate (3·8 grams). The mixture, which darkens gradually, is kept overnight, then treated with ice-water, and the red aqueous layer shaken with animal charcoal. The almost colourless filtrate is freed from dissolved ether by drawing through it a current of air, and on acidifying with dilute acetic acid, a white solid is precipitated which is readily soluble in alcohol. In order to obtain the substance pure for analysis, it is dissolved in the minimum quantity of cold alcohol, and water is added until an emulsion is formed; in a short time almost colourless prisms separate, which, after drying in a vacuum over sulphuric acid, melt at 112—113° to a red liquid, which then solidifies:

0·2050 gave 0·5643 CO_2 and 0·0925 H_2O. C=57·07; H=5·01.
$C_{10}H_8O_2$ requires C=57·00; H=5·00 per cent.

Hydroxymethylenehydrindone gives a deep reddish-violet coloration on the addition of ferric chloride to its alcoholic solution. It is sparingly soluble in cold water, but dissolves readily in dilute alkalis, alkali carbonates, and ammonia, yielding pink solutions. The ammoniacal solution gives with silver nitrate a light brown precipitate, which darkens rapidly with deposition of silver.

The *copper* salt is precipitated on adding an aqueous solution of copper acetate to the hydroxymethylene compound dissolved in alcohol. After a short time, a green solid separates, which is sparingly soluble in hot alcohol, and crystallises on cooling in shining, olive-green plates, decomposing at about 225°:

0·2098 gave 0·0608 CuO. Cu=16·62.
$(C_{10}H_7O_2)_2Cu$ requires Cu=16·66 per cent.

The *benzoate*, $C_9H_6O\colon CH\cdot OBz$, is obtained on shaking a solution of 2-hydroxymethylene-1-hydrindone in excess of dilute sodium hydroxide with benzoyl chloride in the cold; it separates at once as a white solid, which is sparingly soluble in cold, but readily so in hot alcohol, and crystallises from light petroleum (b. p. 60—80°) in colourless, silky needles, melting at 156—157°:

0·2087 gave 0·5907 CO_2 and 0·0849 H_2O. C=77·19; H=4·52.
$C_{17}H_{12}O_3$ requires C=77·27; H=4·55 per cent.

The compound is insoluble in cold dilute potassium hydroxide, but dissolves on boiling with hydrolysis.

The *anilide*, $C_9H_6O\colon CH\cdot NHPh$, is readily formed on adding aniline (0·3 gram) dissolved in dilute acetic acid to a cold concentrated alcoholic solution of the hydroxymethylene compound (0·5 gram). A yellow solid immediately separates; this is moderately soluble in boiling methyl alcohol, and crystallises on cooling in bunches of yellow needles, melting at 217—218°:

0·2106 gave 0·6310 CO_2 and 0·1040 H_2O. C=81·72; H=5·49.
$C_{16}H_{13}ON$ requires C=81·70; H=5·53 per cent.

The anilide is insoluble in water or dilute alkalis, and the alcoholic solution gives no coloration with ferric chloride.

The o-*Aminoanilide*, $C_9H_6O\colon CH{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$.

On mixing alcoholic solutions of 2-hydroxymethylene-1-hydrindone and *o*-phenylenediamine, a deep yellow coloration is developed, with separation of a solid, of which the greater part dissolves in hot alcohol, and crystallises on cooling in bright yellow needles, which begin to darken at 186°, and char at 194°:

0·1908 gave 0·5362 CO_2 and 0·0966 H_2O. C=76·64; H=5·62.
0·2015 ,, 20·4 c.c. N_2 at 22° and 745·5 mm. N=11·23.
$C_{16}H_{14}ON_2$ requires C=76·80; H=5·60; N=11·20 per cent.

Like the anilide and the benzoyl ether, this substance is insoluble in cold dilute alkalis.

The part which is insoluble in alcohol has not been further investigated, but is probably the condensation product formed from two molecules of the hydroxymethylene derivation with one of the diamine, thus: $C_9H_6O\colon CH{\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}CH\colon C_9H_6O$.

The *phenylpyrazole* derivative (XI) is prepared by treating hydroxymethylenehydrindone in concentrated alcoholic solution with phenylhydrazine (1 mol.) dissolved in 60 per cent. acetic acid. After warming on the water-bath, the mixture is diluted with water until a faintly-coloured solid is precipitated. This is dissolved in alcohol, and the solution after decolorisation with animal charcoal is treated with water until it becomes turbid; after some hours the pyrazole separates in beautiful, long, colourless needles, which melt at 124—126° to a red liquid:

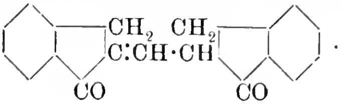
0·2002 gave 0·6065 CO_2 and 0·0935 H_2O. C=82·60; H=5·19.
0·1681 ,, 18·2 c.c. N_2 at 20° and 748 mm. N=12·18.
$C_{16}H_{12}N_2$ requires C=82·76; H=5·17; N=12·07 per cent.

The Semicarbazone (X).—This compound is obtained when an aqueous solution of semicarbazide oxalate (1 gram) is added to a solution of 2-hydroxymethylene-1-hydrindone (1 gram) in methyl alcohol. On keeping, a yellow solid separates, which decomposes on boiling with alcohol, the greater part passing into solution after prolonged heating, whilst an insoluble residue remains. For analysis, therefore, the yellow solid was washed repeatedly with water and with alcohol, and dried first in a vacuum, and then at 100°; when prepared in this way, it is a pale yellow powder, darkening at 205°, and decomposing completely at 211° with evolution of gas:

0·1995 gave 0·4444 CO_2 and 0·0934 H_2O. C=60·75; H=5·09.
0·1745 „ 29·2 c.c. N_2 at 18° and 751 mm. N=19·09.
$C_4H_{11}O_2N_3$ requires C=60·83; H=5·07; N=19·34 per cent.

The substance is readily soluble in potassium hydroxide, and is precipitated slowly on addition of acetic acid.

Ketohydrindylmethyleneketohydrindene,



2-Hydroxymethylene-1-hydrindone, as stated above, begins to change even when heated in the steam-oven, the yellow substance becoming red. The change occurs even more readily on heating to 120—130° in an oil-bath; at this temperature the solid first melts with ebullition to a red liquid, which soon solidifies to the red condensation product. At the same time a pungent liquid distils off; this was collected, and identified as formic acid by the ordinary tests. The red solid which is formed is only sparingly soluble in alcohol and glacial acetic acid, but moderately so in boiling xylene; on cooling, it separates from the latter solvent in deep red needles, which soften at 217°, and melt and evolve gas at 232°:

0·2000 gave 0·6090 CO_2 and 0·0945 H_2O. C=83·04; H=5·25.
0·1974 „ 0·6025 CO_2 „ 0·0910 H_2O. C=83·24; H=5·12.
$C_{19}H_{14}O_2$ requires C=83·21; H=5·11 per cent.

The analytical results, and the fact that formic acid is eliminated in its production, indicate that the substance has the constitution given above. This view is supported by the fact that the compound dissolves in one molecular proportion of potassium hydroxide, yielding a deep red solution, which undoubtedly contains a potassium salt; on the addition of excess of the alkali, this is precipitated as a magenta solid, possessing when dry a metallic lustre.

2-*Hydroxymethylene*-5 : 6-*methylenedioxy*-1-*hydrindone* (V).

On account of the sparing solubility of methylenedioxy-1-hydrindone in ether, attempts have been made to prepare ethoxymethylenemethylenedioxy-1-hydrindone by the method worked out by Claisen for the production of ethyl ethoxymethylenemalonate, namely, by heating the hydrindone with ethyl orthoformate and acetic anhydride. These attempts were unsuccessful, as were also those in which zinc chloride was added to the boiling mixture. In the former case no change occurred; in the latter, some decomposition took place, but the larger proportion of the hydrindone was recovered.

We were therefore obliged to use the same method for the formation of the hydroxymethylene derivative of the methylenedioxyhydrindone as was applied in the case of 1-hydrindone itself; on account of the sparing solubility of methylenedioxy-1-hydrindone in ether, however, dry benzene was employed as a solvent. On adding the mixture of the ketone (8·8 grams) and ethyl formate (3·8 grams) dissolved in benzene to dry sodium ethoxide (3·4 grams) suspended in benzene, a red coloration is developed. After keeping for a day, the mixture is shaken with ice-water, when the suspended solid dissolves; the filtered red aqueous solution is decolorised with animal charcoal, and acidified with dilute acetic acid. A white emulsion is formed, from which a white, crystalline solid separates after several hours. The substance is moderately soluble in alcohol, and the solution, on the addition of water, deposits almost colourless needles, which, after drying in a vacuum, begin to darken at 168°, melting with evolution of gas at 175° to a red liquid, which then solidifies:

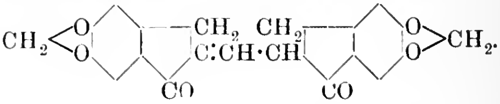
0·1973 * gave 0·4675 CO_2 and 0·0705 H_2O. $C = 64·62$; $H = 3·97$.
$C_{11}H_8O_4$ requires $C = 64·70$; $H = 3·95$ per cent.

The substance dissolves in dilute potassium hydroxide to yield an almost colourless solution. Its alcoholic solution gives an intense green coloration on the addition of ferric chloride, and when treated with an aqueous solution of copper acetate, precipitates a pale green, flocculent solid, which on warming becomes brown.

The *anilide*, $C_{10}H_6O_3$:CH·NHPh, is readily obtained in almost quantitative yield on adding to the alcoholic solution of the hydroxymethylene compound an excess of aniline dissolved in dilute acetic acid. A yellow solid separates at once, which is insoluble in potassium hydroxide; it dissolves sparingly in cold, but moderately in hot, alcohol, and separates on cooling in bunches of yellow needles, which darken at 245°, and char at 279—280°:

0·2565 gave 11·4 c.c. N_2 at 17° and 751 mm. $N = 5·09$.
$C_{17}H_{13}O_3N$ requires $N = 5·02$ per cent.

The Methylenedioxy-derivative of Ketohydrindylmethyleneketohydrindene,



The condensation of hydroxymethylenemethylenedioxy-1-hydrindone to this compound takes place on heating to 160—170°. In this case, also, a red liquid is formed with evolution of formic acid; the

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* Dried in a vacuum.

liquid soon solidifies to a red product, which is insoluble in water and all organic solvents. It is purified, therefore, by washing repeatedly with boiling alcohol, and is then obtained as a red powder, which begins to decompose at 254°, and is completely charred at 264°:

0·1641 gave 0·4194 CO_2 and 0·0567 H_2O. C=69·70; H=3·84.
$C_{21}H_{14}O_6$ requires C=69·61; H=3·86 per cent.

6-*Hydroxymethylene*-1:3-*dimethyl*-Δ^3-cyclo*hexen*-5-*one* (VI).

The action of ethyl formate on dimethyl*cyclo*hexenone occurs under conditions similar to those employed for the preparation of the hydroxymethylene derivatives of the hydrindene series, namely, by adding the mixed solutions of the ester (3·7 grams) and the ketone (6·2 grams) in dry ether to sodium ethoxide (3·4 grams) suspended in ether; the mixture develops a deep red coloration. After keeping overnight, ice-water is added, and the aqueous layer separated and acidified with dilute acetic acid. The brown oil which is obtained, is extracted with ether, and the residue after removal of the ether fractionated in a vacuum. The fraction which boils at 125—128°/15 mm. is redistilled, and the product is then obtained as a yellow oil, boiling at 124—125°/15 mm., and possessing an odour similar to that of the original ketone. It is readily soluble in alcohol, the solution giving an intense reddish-violet coloration on the addition of ferric chloride. It dissolves also in sodium carbonate, yielding a yellow solution, which after a short time turns red; the oil itself darkens on keeping:

0·2099 gave 0·5460 CO_2 and 0·1500 H_2O. C=70·94; H=7·94.
$C_9H_{12}O_2$ requires C=71·05; H=7·89 per cent.

The *copper* salt separates at once on adding an aqueous solution of copper acetate to the hydroxymethylene derivative dissolved in methyl alcohol. After a few hours it is collected, washed with water, and crystallised from methyl alcohol, in which it is readily soluble; on diluting the hot solution with water, it separates as an emulsion, which slowly sets to olive-green, prismatic crystals, melting at 156—157°:

0·2420 gave 0·0520 CuO. Cu=17·14.
$(C_9H_{11}O_2)_2Cu$ requires Cu=17·26 per cent.

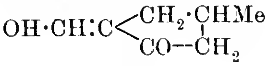
5-*Hydroxymethylene*-3-*methyl*cyclo*pentan*-1-*one* (VII).

The formation of this hydroxymethylene derivative from 3-methyl*cyclo*pentanone and ethyl formate, under the influence of sodium ethoxide, is exactly analogous to the preparation of the hydroxymethylene compounds given above. The brown oil which was obtained distils, on fractionation under diminished pressure, almost entirely at a constant temperature of 77°/12 mm., leaving a slight brown residue. The colourless distillate, on cooling, solidifies to a mass of white crystals, melting at 57—58°. The solid is extremely volatile: 0·2130 gram, when kept in a vacuum desiccator over sulphuric acid, disappeared almost completely in the course of a week:

0·1853 gave 0·4518 CO_2 and 0·1320 H_2O. C=66·50; H=7·91.
$C_7H_{10}O_2$ requires C=66·67; H=7·94 per cent.

The compound dissolves in sodium carbonate, forming a lemon-yellow solution. The solid, on keeping, gradually becomes yellow.

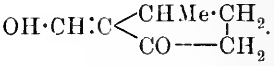
As regards the constitution of the substance, two formulæ are a priori possible, namely:



$OH\cdot CH{:}C\left<\begin{array}{l}CH_2\cdot CHMe\\ CO-CH_2\end{array}\right.$

(VII.)

and



$OH\cdot CH{:}C\left<\begin{array}{l}CHMe\cdot CH_2\\ CO---CH_2\end{array}\right.$.

(VII*a*.)

Since, however, it has been shown (Ruhemann, this vol., p. 1730) that 3-methyl*cyclo*pentanone forms only one condensation product with ethyl oxalate, whereas *cyclo*pentanone itself gives both mono- and di-oxalates, the difference being most probably due to steric hindrance exercised by the methyl group, the formula VII*a* appears improbable.

The *copper* salt is obtained in solution when an aqueous solution of copper acetate is added to an alcoholic solution of the hydroxymethylene compound. It is very soluble in water and dilute alcohol, forming deep-green solutions.

The *anilide*, $C_6H_8O{:}CH\cdot NHPh$, separates as an oil when aniline, dissolved in dilute acetic acid, is added to the alcoholic solution of the hydroxymethylene derivative; after a short time, the oil sets to a solid, which is readily soluble in hot alcohol. On diluting the alcoholic solution with water, an emulsion is formed, which soon sets to faintly yellow, prismatic needles, melting at 118—119°. The anilide is insoluble in dilute potassium hydroxide:

0·2051 gave 0·5835 CO_2 and 0·1354 H_2O. C=77·59; H=7·34.
$C_{13}H_{15}ON$ requires C=77·61; H=7·46 per cent.

We are at present engaged in the further study of the condensation products formed under the influence of heat from the hydroxymethylene derivatives of the hydrindene series. We are also attempting to ascertain to what extent the same condensation can be effected in the case of other hydroxymethylene derivatives.

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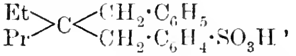
CCLXV.—*A Study of Some Organic Derivatives of Tin as Regards their Relation to the Corresponding Silicon Compounds.*

By Thomas Alfred Smith, B.Sc., A.I.C., and
Frederic Stanley Kipping.

In spite of the well-established relationship between organic derivatives of silicon and analogous derivatives of carbon, as regards their general behaviour, there are many noteworthy instances in which a silicon compound differs very considerably in certain particulars from the corresponding carbon compound of the same type; consequently, any forecast of the course of a reaction in the case of a compound of the one element, which is based on a knowledge of the behaviour of the corresponding derivative of the other, may be partly or entirely unfulfilled.

It would also seem that a similar lack of success may attend an attempt to predict the reactions of an organic derivative of tin from analogy to those of the corresponding compound of silicon; at any rate, this is one of the lessons that we have been taught by the results of the work described in this paper.

For some time past, intermitted efforts have been made in these laboratories to prepare an asymmetric carbon compound of the same type as that of one of the silicon compounds which has been resolved into its optically active components; if this task could be accomplished, and the *dl*-compound,



$$\begin{matrix}\mathrm{Et} \\ \mathrm{Pr}\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot C_6H_5 \\ CH_2\cdot C_6H_4\cdot SO_3H\end{matrix},$$

for example, could be obtained and resolved, a comparison of the optical properties of the active acid with those of the corresponding silicon compound (Challenger and Kipping, Trans., 1910, **97**, 755) might lead to important conclusions.

Hitherto the experiments in this direction have been fruitless; thus, although the preparation of the silicon compound,

$$SiEtPr(CH_2\cdot C_6H_5)_2,$$

is a relatively easy matter (Challenger and Kipping, Trans., 1910, **97**, 142), that of dibenzylethylpropylmethane presents far greater difficulties, owing to the fact that substances of the type CR_3X so readily lose the elements of a halogen acid, HX, when the displacement of the halogen by a hydrocarbon radicle is attempted (Kipping and Davies, Trans., 1911, **99**, 300).

The possibility of obtaining a tin compound, analogous to one of the known optically active derivatives of silicon, was therefore considered, and experiments were instituted on the preparation of a dibenzylethylpropylstannane * of the composition

$$SnEtPr(CH_2 \cdot C_6H_5)_2,$$

corresponding with dibenzylethylpropylsilicane, by the following series of reactions:

$$SnCl_4 + 2MgCl \cdot CH_2 \cdot C_6H_5 = SnCl_2(CH_2 \cdot C_6H_5)_2 + 2MgCl_2.$$
$$SnCl_2(CH_2 \cdot C_6H_5)_2 + MgEtBr = SnClEt(CH_2 \cdot C_6H_5)_2 + MgClBr.$$
$$SnClEt(CH_2 \cdot C_6H_5)_2 + MgPrBr = SnEtPr(CH_2 \cdot C_6H_5)_2 + MgClBr.$$

If this product could be converted into a *dl*-sulphonic acid, analogous to dibenzylethylpropylsilicanesulphonic acid, and the *dl*-tin compound could then be resolved, the desired object would have been attained.

Certain stages of the proposed plan were accomplished with comparative facility, although by methods somewhat different from those originally outlined, which were based on previous experience with the corresponding silicon compounds. In the first place, the dibenzylstannic chloride, $SnCl_2(CH_2 \cdot C_6H_5)_2$, with which the work was to commence, could not be conveniently obtained directly from stannic chloride by a process similar to that used in the preparation of dibenzyldichlorosilicane (Robison and Kipping, Trans., 1908, **93**, 451), because when stannic chloride was treated with two molecular proportions of magnesium benzyl chloride, the main product was tribenzylstannic chloride, and a considerable quantity of the stannic chloride remained unchanged. It was much simpler, therefore, to prepare the tribenzyl derivative (for which purpose three, instead of two, molecular proportions of magnesium benzyl chloride were used) and then to displace one of the benzyl-groups in the product by halogen, than to isolate the small proportion of the dichloride which was formed when two equivalents of the Grignard reagent were employed.

The conversion of the tribenzylstannic chloride into the dibenzyldichloro-derivative was accomplished with the aid of iodine, the reaction taking place in accordance with the following equation:

$$2Sn(CH_2 \cdot C_6H_5)_3Cl + 2I_2 = Sn(CH_2 \cdot C_6H_5)_2Cl_2 + Sn(CH_2 \cdot C_6H_5)_2I_2 + 2C_6H_5 \cdot CH_2I.$$

The dibenzyldi-iodostannane, which was simultaneously formed, was also transformed into the dichloride through the corresponding oxide.

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* The suggestion is here made that the name "*stannane*" should be used in preference to the rather cumbersome "*stannimethane*" to denote the unknown hydride, SnH_4, of which many of the simple tin derivatives may be regarded as derivatives.

Although a very satisfactory yield of dibenzyldichlorostannane was thus obtained, the relative ease with which the tribenzyl derivative could be prepared, and the readiness with which a benzyl group could be displaced by iodine, suggested a modification of the original plan; instead of attempting to substitute first an ethyl and then a propyl group for the two atoms of chlorine in the dichloride, it seemed better to start from tribenzylstannic chloride and try to carry out the series of operations shown by the following equations:

$$\text{I. } Sn(CH_2{\cdot}C_6H_5)_3Cl + MgEtBr = SnEt(CH_2{\cdot}C_6H_5)_3 + MgClBr.$$

$$\text{II. } SnEt(CH_2{\cdot}C_6H_5)_3 + I_2 = SnEtI(CH_2{\cdot}C_6H_5)_2 + C_6H_5{\cdot}CH_2I.$$

$$\text{III. } SnEtI(CH_2{\cdot}C_6H_5)_2 + MgPrBr = SnEtPr(CH_2{\cdot}C_6H_5)_2 + MgBrI.$$

That the changes represented by I and III would occur was, of course, very probable, since many compounds of the type SnR_4 have already been prepared by such interactions, but whether or not the substitution expressed by II could be realised was somewhat doubtful. For although the above-mentioned experiments had proved that the benzyl group could be easily eliminated with the aid of iodine, the fact that alkyl groups may be displaced in a similar manner had also been established; moreover, in the case of those compounds which contain two or more different hydrocarbon radicles, it would seem that the course of the reaction cannot be foretold; thus, whereas it was shown by Cahours (*Annalen*, 1862, **122**, 59) that trimethylethylstannane is decomposed by iodine with separation of ethyl iodide, it was found by Pope and Peachey (Proc., 1900, **16**, 42) that both trimethylethyl- and dimethylethylpropyl-stannane are decomposed with the formation of methyl iodide, the alkyl of lower or lowest molecular weight being separated from the tin atom. In the light of these observations, it seemed possible, or even probable, that the action of iodine on tribenzylethylstannane might give rise to tribenzylstannic iodide and ethyl iodide.

Experiment showed, however, that the reaction expressed by equation II could be brought about, and dibenzylethylpropylstannane was, in fact, obtained in accordance with the above scheme.

It was at the next stage that the difference between dibenzylethylpropylstannane and dibenzylethylpropylsilicane became sufficiently pronounced to defeat entirely the object of this work. When attempts were made to sulphonate one of the benzyl groups in the tin derivative, a complex reaction occurred, and even when chlorosulphonic acid was used at low temperatures, both the benzyl groups were eliminated, with the formation, among other products, of a salt of ethylpropylstannic oxide.

Many sulphonation experiments were made, not only with dibenzylethylpropylstannane, but also with dibenzyldiethylstannane, which was more easily prepared than the ethylpropyl compound; they all ended in failure. These two compounds, apparently, unlike dibenzylethylpropylsilicane, cannot be converted into their monosulphonic derivatives owing to the readiness with which the benzyl group is eliminated.

The union between the benzyl group and the tin atom shows, in fact, the same instability towards sulphuric acid as that between the phenyl group and the silicon atom (Kipping, Trans., 1907, **91**, 212); the union between the benzyl group and the silicon atom, on the other hand, is much more resistant to the action of sulphonating agents, as has been shown by the isolation of several substances containing the group $>Si\cdot CH_2\cdot C_6H_4\cdot SO_3H$. The breakdown of the analogy between dibenzylethylpropylstannane and dibenzylethylpropylsilicane, in so far as concerns their behaviour towards sulphonating agents, brought this work to an abrupt conclusion; it is intended, nevertheless, to utilise some of the compounds which have been obtained for further experiments on the preparation of some *dl*-derivatives of tin.

EXPERIMENTAL.

Preparation of Tribenzylstannic Chloride, $Sn(CH_2\cdot C_6H_5)_3Cl$.

Tribenzylstannic chloride was first prepared by Pfeiffer and Schnurmann (*Ber.*, 1904, **37**, 319) by the gradual addition of stannic chloride (1 mol.) to an ice-cold ethereal solution of magnesium benzyl chloride (3 mols.). Under these conditions the yield was very poor, the weight of solid raw material amounting to only 20 per cent. of the theoretical, and that of the pure compound to only about 8 per cent.

Much more satisfactory results are obtained by omitting the preliminary preparation of the solution of the Grignard reagent (compare Kipping and Davies, Trans., 1911, **99**, 296), and carrying out the operation in the following manner: Some ether (about 10 vols.), contained in a flask, is cooled in ice and stannic chloride (100 grams, 1 vol.) is slowly added from a tap funnel; during this operation the mixture is vigorously stirred, and atmospheric moisture is excluded. In this way the solid additive product of ether and stannic chloride which is formed is obtained in a very finely divided condition. Dry magnesium powder (28 grams, 3 atoms) is now added, and a little benzyl chloride is dropped into the mixture from a tap funnel; if the reaction does not start in the course of a few minutes, it is caused to do so by the addition of a small quantity of magnesium benzyl chloride prepared in a test-tube. The rest of the benzyl chloride (150 grams, 3 mols.) is then slowly dropped in, an operation which occupies about two hours, whilst the contents of the flask are vigorously stirred and cooled in ice. When this process is at an end, and the development of heat is no longer noticed, the mixture is heated on a water-bath under a reflux condenser during two hours. The ether is then distilled off, and the product is heated during a further period of two hours at about 100°. When cold, the solid contents of the flask are slowly added to a large volume of water, and the crude tribenzylstannic chloride is separated and washed with water. The preparation is first crystallised from acetone, containing a little water, and then from glacial acetic acid, until its melting point is constant. The yield of pure substance, melting at 143—145°, is about 60 per cent. of the theoretical:

A sample dried over sulphuric acid was analysed:

0·2969 gave 0·0980 AgCl. Cl = 8·16.

$C_{21}H_{21}ClSn$ requires Cl = 8·29 per cent.

Tribenzylstannic chloride is very readily soluble in acetone, benzene, or chloroform, less readily so in ether or alcohol, and insoluble in water; it crystallises from boiling glacial acetic acid in fairly well-defined prisms.

Dibenzylstannic Chloride, $SnCl_2(CH_2{\cdot}C_6H_5)_2$.

A small quantity of dibenzylstannic chloride may be isolated from the residues obtained in the preparation of the tribenzyl derivative, and by employing two instead of three molecular proportions of magnesium benzyl chloride, the yield of the dibenzyl compound may be increased. Even under the more favourable conditions, however, the main product of the reaction is tribenzylstannic chloride, and a considerable proportion of stannic chloride remains unchanged. It is more convenient, therefore, to prepare the dibenzyl- from the tribenzyl-derivative in the following manner:

Tribenzylstannic chloride (1 mol.) is dissolved in warm carbon tetrachloride, and iodine (1 mol.) is added in small portions at a time to the warm solution, which is vigorously shaken; the reaction represented by the following equation then takes place:

$$2Sn(CH_2{\cdot}C_6H_5)_3Cl + 2I_2 = Sn(CH_2{\cdot}C_6H_5)_2Cl_2 + Sn(CH_2{\cdot}C_6H_5)_2I_2 + 2C_6H_5{\cdot}CH_2I.$$

At first the colour of the iodine rapidly disappears, but towards the end of the operation the reaction takes place much more slowly, and it may be necessary to heat the solution in order to complete the change. Direct sunlight also accelerates the change very considerably. When the colour of the iodine has entirely disappeared, the solution is placed aside, and the crystals of dibenzylstannic chloride which are afterwards deposited are collected by the aid of the pump, and washed with a little light petroleum. The substance is then recrystallised from acetone containing a little hydrochloric acid.

The mother liquors, which contain the di-iodide and some dichloride, together with benzyl iodide, are best treated in the following way: The solvent and the benzyl iodide are removed by distillation in a current of steam, and the residue is then well shaken with a concentrated aqueous solution of ammonium hydroxide. The solid dibenzylstannic oxide, which is thus formed, is well washed with water to free it from ammonium salts, and is then dissolved in a mixture of acetone and concentrated hydrochloric acid; from this solution dibenzylstannic chloride is deposited in colourless crystals. The total yield of the chloride is practically theoretical.

A sample dried over sulphuric acid was analysed:

0·1515 gave 0·1170 AgCl. Cl = 19·07.

$C_{14}H_{14}Cl_2Sn$ requires Cl = 19·08 per cent.

Dibenzylstannic chloride is readily soluble in acetone, alcohol, ether, carbon tetrachloride, or chloroform, but it is only sparingly soluble in hot light petroleum; it dissolves freely in boiling acetic acid, and separates from the cooled solution in long needles melting at 163—164°.

Dibenzylstannic Iodide, $Sn(CH_2{\cdot}C_6H_5)_2I_2$.

The dibenzylstannic iodide which is formed in the preparation of dibenzylstannic chloride by the method just described is more soluble than the dichloride in carbon tetrachloride, and therefore remains in the mother liquors from which the last-named compound has been deposited. If the solvent and the benzyl iodide are removed by distillation in a current of steam, and the residue is then recrystallised, first from alcohol, and then several times from ether and petroleum, the di-iodide is finally obtained in a pure condition.

A sample dried over sulphuric acid was analysed:

0·3860 gave 0·3261 AgI. I = 45·67.

$C_{14}H_{14}I_2Sn$ requires I = 45·75 per cent.

Dibenzylstannic iodide crystallises in long, silky, yellow needles, melting at 86—87°; its behaviour towards solvents is much the same as that of the dichloride, but, as stated above, the di-iodide is the more soluble in carbon tetrachloride.

Dibenzylstannic iodide may also be obtained by dissolving the oxide in a hot mixture of acetone and hydriodic acid, and then leaving the solution to crystallise.

Dibenzylstannic Bromide, $Sn(CH_2{\cdot}C_6H_5)_2Br_2$.

Dibenzylstannic bromide is formed when dibenzylstannic oxide is treated with hydrobromic acid in acetone solution; the product is crystallised from aqueous alcohol, and then from light petroleum; it forms colourless needles, melts at 130°, and resembles the chloride in its behaviour towards solvents, but is more soluble than that compound:

0·2845 gave 0·2316 AgBr. Br = 34·7.

$C_{14}H_{14}Br_2Sn$ requires Br = 34·7 per cent.

Dibenzylstannic Acetate, $Sn(CH_2{\cdot}C_6H_5)_2(O{\cdot}CO{\cdot}CH_3)_2$.

This salt is easily obtained by dissolving the oxide in hot glacial acetic acid; when the solution is cooled or diluted with water, the acetate separates in long, colourless needles, which may be recrystallised from aqueous alcohol.

The sample for analysis was dried over sulphuric acid:

0·1501 gave 0·2833 CO_2 and 0·0644 H_2O. C = 51·5; H = 4·77.
0·1576 ,, 0·2964 CO_2 ,, 0·0686 H_2O. C = 51·3; H = 4·83.

$C_{18}H_{20}O_4Sn$ requires C = 51·5; H = 4·8 per cent.

Dibenzylstannic acetate melts at 136—137°, and is readily soluble in acetone, alcohol, benzene, or chloroform; like the dichloride and other salts of dibenzylstannic oxide, it dissolves slowly in an aqueous solution of potassium hydroxide, giving a product from which the oxide may be precipitated with the aid of carbon dioxide.

Tetrabenzylstannane, $Sn(CH_2{\cdot}C_6H_5)_4$.

Tetrabenzylstannane is easily obtained by gradually adding benzyl chloride (4 mols.) to an ethereal solution of stannic chloride (1 mol.) in the presence of powdered magnesium (4 atoms).

The ethereal solution of the stannic chloride is prepared as described above (p. 2556), the reaction is started in the usual manner, and when the whole of the benzyl chloride has been added, the ether is distilled off, and the residue is heated at 100° during two to three hours. The cold mixture is treated with water, and submitted to steam distillation in order to remove any dibenzyl and unchanged benzyl chloride; the solid residue is then separated by the aid of the pump, dried on porous earthenware, and dissolved in light petroleum. When this solution is cooled in ice, the tetrabenzyl derivative is deposited in colourless crystals, which are easily purified by recrystallisation from light petroleum.

The sample for analysis was dried over sulphuric acid:

0·2505 gave 0·6364 CO_2 and 0·1316 H_2O. C = 69·29; H = 5·84.
0·2505 „ 0·0803 SnO_2. Sn = 25·2.

$C_{28}H_{28}Sn$ requires C = 69·54; H = 5·79; Sn = 24·64 per cent.

Tetrabenzylstannane crystallises in well-defined prisms, and melts at 42—43°. It is readily soluble in most of the common organic solvents, with the exception of light petroleum. Like many of the benzyl derivatives of tin, tetrabenzylstannane slowly undergoes atmospheric oxidation, even at the ordinary temperature, with formation of benzaldehyde.

Tribenzylethylstannane, $SnEt(CH_2{\cdot}C_6H_5)_3$.

Tribenzylethylstannane is readily formed with development of heat when tribenzylstannic chloride is treated with excess of an ethereal solution of magnesium ethyl bromide, which is slowly added from a tap funnel. When the whole of the Grignard reagent has been run in, the ether is distilled off, and the solid residue is heated at 100° during two to three hours; the product is then cooled and treated with water. The tin compound, which floats at the surface in the form of an oil, is transferred to a separating funnel, and washed first with dilute sulphuric acid and then with water; it is afterwards dissolved in ether and dried with the aid of calcium chloride. When the ethereal solution is allowed to evaporate spontaneously, the tribenzylethylstannane is deposited in glistening plates; it is recrystallised several times from a mixture of alcohol and light petroleum, cooled in ice. An almost theoretical yield of the compound is thus obtained, and its purity is indicated by the following analysis of a sample which had been dried over sulphuric acid:

0·2324 gave 0·0833 SnO_2. Sn = 28·24.

$C_{23}H_{26}Sn$ requires Sn = 28·25 per cent.

Tribenzylethylstannane separates from alcoholic light petroleum in colourless, tabular crystals, and melts at 31—32°. It is readily soluble in ether, benzene, or chloroform, but is somewhat less soluble in alcohol and sparingly so in light petroleum. It undergoes atmospheric oxidation at the ordinary temperature, and gives benzaldehyde; when heated under atmospheric pressure it is decomposed with separation of tin.

Dibenzyldiethylstannane, $SnEt_2(CH_2·C_6H_5)_2$.

Dibenzyldiethylstannane may be prepared by treating dibenzylstannic chloride with excess of magnesium ethyl bromide in ethereal solution. The operation is carried out exactly as described in the case of the tribenzylethyl derivative, and when water has been added the ethereal solution is separated, washed, and dried with calcium chloride. It is then distilled under a pressure of 20 mm., and the portion boiling at 223—224°, which is practically the whole of the crude oil, is collected separately; a very small proportion is decomposed during distillation, with separation of tin:

0·1881 gave 0·4113 CO_2 and 0·1163 H_2O. C=59·63; H=6·87.
0·5073 „ 0·2118 SnO_2. Sn=32·9.
$C_{18}H_{24}Sn$ requires C=60·1; H=6·7; Sn=33·1 per cent.

Dibenzyldiethylstannane is a colourless oil specifically heavier than water, and it does not solidify at the ordinary temperature; it is miscible with all the common organic solvents; when heated under atmospheric pressure it is rapidly decomposed, giving a deposit of tin, and it is readily oxidised on exposure to the air, with formation of benzaldehyde.

Dibenzylethylpropylstannane, $SnEtPr(CH_2·C_6H_5)_2$.

Dibenzylethylpropylstannane may be obtained from tribenzylethylstannane in the following manner: Tribenzylethylstannane (1 mol.) is dissolved in carbon tetrachloride, and iodine (1 mol.) is added in small portions at a time, when the following reaction takes place:

$$SnEt(CH_2Ph)_3 + I_2 = SnEt(CH_2Ph)_2I + CH_2PhI.$$

The action of the iodine is facilitated by warming the solution or by exposing it to direct sunlight. When the theoretical quantity of the halogen has been added, the solvent and the benzyl iodide are removed with a current of steam, and the crude oily dibenzylethylstannic iodide is extracted with ether. The residue obtained by the evaporation of the dried ethereal solution does not crystallise, and decomposes when it is heated under diminished pressure; it is therefore treated directly with one molecular proportion of magnesium propyl bromide in the usual manner, and, after the ether has been distilled, the residue is heated at about 140° during one hour. To the cold product water is added, the oily layer of dibenzylethylpropylstannane is dissolved in ether, and the washed ethereal extract is dried and evaporated. The product is then distilled under a pressure of 15 mm. The fraction boiling at 220—225° forms about 70 per cent. of the crude product, and is pure dibenzylethylpropylstannane, as shown by the following analyses:

0·2221 gave 0·4975 CO_2 and 0·1422 H_2O. C=61·1; H=7·1.
0·2569 „ 0·5748 CO_2 „ 0·1625 H_2O. C=61·0; H=7·0.
$C_{19}H_{26}Sn$ requires C=61·1; H=7·0 per cent.

Dibenzylethylpropylstannane does not solidify even at 0°; it oxidises in the air at the ordinary temperature with the formation of benzaldehyde, and when heated under atmospheric pressure it decomposes, giving a deposit of tin. It is miscible with all the ordinary solvents.

Attempts to Obtain a Monosulphonic Derivative of Dibenzylethylpropyl- and of Dibenzyldiethyl-stannane.

On the addition of dibenzyldiethylstannane to concentrated sulphuric acid cooled in ice, the oil slowly dissolves, and when the slightly coloured liquid is poured into ice-cold water, a clear solution is obtained; this solution, however, has the unpleasant odour of the diethylstannic salts, and when treated with excess of a solution of ammonium hydroxide it gives a large quantity of a white precipitate. This precipitate is diethylstannic oxide; on treatment with hydrochloric acid, it passes into solution, forming diethylstannic chloride, which may be extracted with ether, and finally obtained in crystals melting at 80—81°. A sample of the dichloride thus obtained was mixed with some diethylstannic chloride from another source, and the melting point of the mixture was the same as that of the separate preparations. An examination of the ammoniacal solution, from which the diethylstannic oxide had been separated, failed to reveal the presence of any sulphonic acid containing tin, and, judging from the quantity of diethylstannic oxide which had been formed, it was obvious that normal sulphonation had not taken place.

On the addition of chlorosulphonic acid, diluted with carbon tetrachloride, to dibenzyldiethylstannane dissolved in the same solvent and cooled in a freezing mixture, a certain amount of charring is observed, and a brown oil is deposited, but no evolution of hydrogen chloride occurs. If when one molecular proportion of the chlorosulphonic acid has been added the solution is filtered from suspended oil and then allowed to evaporate at the ordinary temperature, crystals of diethylstannic chloride are deposited. The oil which separates from the carbon tetrachloride solution also consists principally of a salt of diethylstannic oxide; when treated with water, it gives a solution which shows the reactions of a sulphate, and with ammonium hydroxide it gives diethylstannic oxide, which is readily identified by converting it into the corresponding dichloride.

Although most of the attempts to prepare a sulphonic derivative were made with dibenzyldiethylstannane, some experiments were also carried out with dibenzylethylpropylstannane; the behaviour of the latter, however, was in all respects analogous to that of the diethyl derivative, inasmuch as it was decomposed with formation of a salt of ethylpropylstannic oxide.

Ethylpropylstannic Chloride, $SnEtPrCl_2$.

Ethylpropylstannic chloride was obtained from the products of the action of concentrated sulphuric acid and chlorosulphonic acid on dibenzylethylpropylstannane. When the aqueous solution of the product of sulphonation was treated with ammonium hydroxide it gave a white precipitate, which was separated by filtration, and dissolved in hydrochloric acid; the acid solution was then extracted with ether, and the extract evaporated. In this way the dichloride was obtained in needles having an unpleasant odour, resembling that of the diethylstannic salts.

Ethylpropylstannic chloride crystallises well from light petroleum, in which it is only sparingly soluble in the cold, and melts at 57—58°; it is readily soluble in ether, alcohol, or water. A chlorine estimation was made by boiling the substance with excess of ammonium hydroxide, filtering from the precipitated ethylpropylstannic oxide, and then estimating the halogen in the filtrate by precipitation with silver nitrate and nitric acid:

0·5439 gave 0·5925 AgCl. Cl = 27·1.

$C_5H_{12}Cl_2Sn$ requires Cl = 27·1 per cent.

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Nottingham.

CCLXVI.—*Contributions to the Chemistry of the Terpenes. Part XV. Synthesis of a Menthadiene from Carvacrol.*

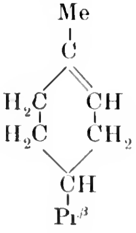
By George Gerald Henderson and
Schachno Peisach Schotz, B.Sc.

The synthesis of a menthadiene from thymol has been described in a previous paper (Henderson and Boyd, Trans., 1911, **99**, 2159). The several steps in the process then adopted were briefly: (1) the preparation of hexahydrothymol, $C_{10}H_{19}\cdot OH$, from thymol, $C_{10}H_{13}\cdot OH$, according to the method of Sabatier and Senderens; (2) the elimination of the elements of water from hexahydrothymol, with formation of Δ^3-menthene, $C_{10}H_{18}$; (3) the preparation of menthene dibromide; and (4) the conversion of the dibromide into a menthadiene, $C_{10}H_{16}$, by elimination of two molecules of hydrogen bromide. It appeared of interest to ascertain if the same menthadiene or an isomeride would be produced from carvacrol by a similar series of reactions, and accordingly the experiments described in the present paper were carried out.

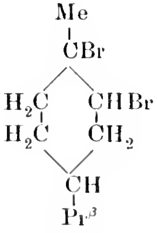
Kondakoff and Schindelmeiser (*J. pr. Chem.*, 1905, [ii], **72**, 193; 1907, **75**, 141) have described the synthesis of a menthadiene from carvomenthyl chloride. This compound was converted, successively, into carvomenthene, *tert.*-carvomenthol, *tert.*-carvomenthyl chloride, *tert.*-carvomenthene, and carvomenthene dibromide. The dibromide, on treatment with alcoholic potassium hydroxide, yielded a hydrocarbon, which could be separated into two fractions; the larger boiled at 175—180°, and had D_4^{20} 0·825 and n_D 1·46693, the smaller boiled at 180—185°, and had D_4^{20} 0·828 and n_D 1·4673; molecular refraction found 45·22, calculated for $C_{10}H_{16}|^{=}2$ 45·56. This hydrocarbon, or mixture of hydrocarbons (b. p. 176—185°), yielded a "nitrosite" in two crystalline modifications, which appeared very similar to the nitrite of β-phellandrene, and it was therefore concluded that β-phellandrene had been obtained synthetically.

If none of the reactions involved in each of the two synthetic processes had the effect of inducing intramolecular rearrangement, the menthadiene obtained by our method ought to have been identical with that prepared by Kondakoff and Schindelmeiser. This was not the case, but the reason for the difference in results remains obscure for the present.

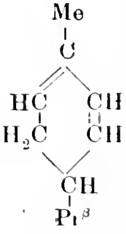
The menthene which we obtained by the dehydration of hexahydrocarvacrol (carvomenthol) was apparently the Δ^1-isomeride (formula I), and the dibromide which it yielded should therefore be 1:2-dibromomenthane (formula II). Hence it was to be expected that, by elimination of hydrogen bromide from this compound, either $\Delta^{1:5}$-menthadiene (α-phellandrene, formula III) or $\Delta^{1(7):2}$-menthadiene (β-phellandrene, formula IV) would be obtained:



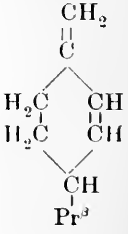
(I.)



(II.)



(III.)



(IV.)

Both *α*- and *β*-phellandrene, however, yield characteristic crystalline nitrites, whilst all attempts to prepare a nitrite from our menthadiene were unsuccessful. This leads to the conclusion that the constitution of our product is different from that of either of the phellandrenes. If that is the case, it is evident that either the process of eliminating hydrogen bromide from the menthene dibromide, or, more probably, the formation of the dibromide from Δ^1-menthene, must have been attended by intramolecular rearrangement.

The physical properties of the menthadiene which we obtained from carvacrol through the dibromide of Δ^1-menthene are very similar to those of the hydrocarbon formerly prepared from thymol through the dibromide of Δ^3-menthene. The former, however, appears to undergo change much more rapidly on exposure to air, and, on the whole, to be a different terpene; its constitution remains a matter for further investigation.

EXPERIMENTAL.

Carvacrol was converted into carvomenthol by hydrogenation in presence of finely-divided nickel, the method being based on that described by Brunel (*Ann. Chim. Phys.*, 1905, [viii], **6**, 205). The tube containing the nickel was maintained at a temperature of about 130°, and the hydrogen was passed at the rate of about 50 c.c. per minute. The product, which distilled over slowly in the form of a colourless, viscous liquid of agreeable odour, was dissolved in ether, the ethereal solution agitated with small quantities of aqueous sodium hydroxide until the traces of unchanged carvacrol had been removed, and then washed with water and dried with anhydrous sodium sulphate, the ether evaporated, and the residual liquid distilled. The bulk passed over between 214° and 223°, a small fraction distilling below 200°, and a little of a tarry residue remaining in the flask. The principal fraction was mixed with rather more than the calculated quantity of phthalic anhydride, and heated at 120° for several hours. The product whilst still warm was poured into a slight excess of dilute aqueous sodium carbonate, and when all was dissolved the solution was agitated repeatedly with light petroleum until the carvomenthone (which is produced in small quantity along with the carvomenthol) had been removed. On acidification of the aqueous solution the hydrogen phthalate of carvomenthol was precipitated in the form of a pasty mass, which became crystalline when left in contact with the mother liquor. The small, white crystals were collected, washed with water, and finally heated for several hours under a reflux condenser with alcoholic sodium hydroxide. The liberated carvomenthol was distilled over in a current of steam, separated from the distillate by means of ether, and, after evaporation of the ether, purified by distillation, practically the whole passing over at 220—222°.

In order to effect dehydration the purified carvomenthol was mixed with about three times its weight of anhydrous oxalic acid, and heated for several days in a flask provided with an air condenser at such a temperature that the mixture was kept gently boiling. When the process appeared to be completed the contents of the flask were distilled in a current of steam. A colourless liquid passed over rapidly, and when denser, oily drops began to appear the distillation was interrupted. After cooling, the contents of the distillation flask were agitated with ether, the ethereal solution dried with anhydrous sodium sulphate, and the residue left on evaporation of the ether again heated with oxalic acid. The liquid which had passed over with the steam was separated with the aid of ether, the ethereal solution dried, the ether removed, and the residue distilled. The fraction which passed over at 173—177° was collected and redistilled, and the portion of higher boiling point was again heated with oxalic acid. In this way the carvomenthene was obtained in the form of a colourless liquid with a pleasant odour; it had the following constants: boiling point, 173—175°, at atmospheric pressure; D_4^{20} 0·819; n_D 1·45510; molecular refraction found, 45·72; calculated for $C_{10}H_{18}$ = 45·63. The physical properties of the hydrocarbon agree closely with those of Δ^1-menthene, which was obtained by Wallach in two ways, namely, (1) from carvomenthol by treatment with potassium hydrogen sulphate (*Annalen*, 1893, **277**, 132), and (2) from *tert.*-carvomenthol (1-hydroxymenthane) by heating with anhydrous zinc chloride (*Annalen*, 1911, **381**, 58).

In order to obtain the dibromide, the menthene was dissolved in ten times its weight of glacial acetic acid, and a solution of slightly more than the calculated quantity of bromine in the same solvent slowly added from a dropping funnel; during the process the flask was cooled with ice and the liquid stirred continuously. The product was poured into water, and the menthene dibromide, $C_{10}H_{18}Br_2$, which separated as a heavy, oily liquid, extracted with ether. The ethereal solution was washed and dried, the ether removed, and a small quantity of the residual liquid distilled under diminished pressure. The bulk passed over at about 140°/22 mm. in the form of a colourless, somewhat viscous liquid with an unpleasant odour, which did not solidify even when strongly cooled. It is susceptible to the action of air, quickly acquiring a green colour, and as it undergoes a certain amount of decomposition when distilled, the greater part of our preparation was converted into the menthadiene without previous distillation.

The menthadiene was prepared from the dibromide by two different methods, which, however, gave practically the same results. The principle of the first of these is due to Wallach (*Annalen*, 1887, **239**, 3). A mixture of one part of the dibromide, one and a-half parts of anhydrous sodium acetate, and three parts of glacial acetic acid was boiled gently for an hour on the sand-bath in an atmosphere of carbon dioxide. It was then distilled in a current of steam, and the distillate was made strongly alkaline with potassium hydroxide, heated for an hour on the water-bath, and again distilled in steam. The liquid which passed over was separated from the condensed water by means of ether, the ethereal solution dried, the ether removed, and the residue distilled under diminished pressure in an atmosphere of dry carbon dioxide. In this process a certain amount of resinification occurs, and the following alternative method was found to be preferable on the whole. The dibromide (1 mol.) was heated on a water-bath under a reflux condenser with alcoholic potassium hydroxide (4 mols.) until no further separation of potassium bromide occurred. On account of the tendency of the menthadiene to undergo oxidation, it was found advantageous to carry out the operation in an atmosphere of hydrogen. The mixture was then distilled in a current of steam, and the distillate agitated several times with light petroleum. The petroleum solution was thoroughly washed with water, dried with anhydrous calcium chloride, and distilled.

The substance thus obtained from menthene dibromide was distilled under diminished pressure in an atmosphere of dry carbon dioxide, and yielded two liquid fractions, one boiling below 90°, and the other above 100°/20 mm. The latter on treatment with sodium reacted vigorously, and formed a sodium derivative, which was decomposed on treatment with water. On redistillation under atmospheric pressure it yielded a fraction which boiled at 204—206°. This was a somewhat viscous, colourless liquid with a strong odour, which quickly reduced an alkaline solution of potassium permanganate and united rather slowly with bromine. Analysis gave results which indicated that it was largely composed of a compound of the formula $C_{10}H_{18}O$, possibly an unsaturated alcohol. It was not further examined.

The lower fraction, a liquid of a yellow colour, was fractionally distilled over sodium, in a current of dry hydrogen, until no further action took place. It was found that unless the air in the distilling apparatus was displaced by hydrogen the distillate always had a yellow colour. Finally, a fraction of constant boiling point was obtained. The menthadiene thus prepared is a colourless liquid, slightly oily, and with an odour reminiscent of other terpenes. It has the following constants: boiling point, 172—174°, at atmospheric pressure; D_4^{20} 0·8272, n_D 1·46430; molecular refraction found 45·36, calculated for $C_{10}H_{16}|\overline{2}$ 45·24. It is unsaturated, at once reducing an alkaline solution of potassium permanganate and uniting additively with bromine, but it does not appear to be capable of forming a tetrabromide, for when treated with bromine dissolved in dry chloroform at the ordinary temperature, evolution of hydrogen bromide begins if more than two atomic proportions of bromine are added. A solution of the hydrocarbon in acetic anhydride assumes a raspberry-red colour on addition of a few drops of concentrated sulphuric acid. On exposure to air it absorbs oxygen readily, especially if hot. Several attempts to prepare a nitrite were made, strictly according to the method used by Wallach (*Annalen*, 1895, **287**, 373) for the preparation of phellandrene nitrite but no crystalline compound could be isolated; indeed, nitrous acid appeared to have little or no action on the hydrocarbon. Analysis confirmed the formula $C_{10}H_{16}$. (Found, C=87·8; H=12·1. Calc., C=88·2; H=11·8 per cent.)

We gladly take this opportunity of expressing our thanks to the Research Fund Committee of the Carnegie Trust for a grant which defrayed the expense of this work.

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INDEX OF AUTHORS' NAMES.

TRANSACTIONS AND PROCEEDINGS. 1912.

(Marked T. and P. respectively.)

INDEX OF SUBJECTS.

TRANSACTIONS AND PROCEEDINGS. 1912.

(Marked T. and P. respectively.)

Single organic compounds of known empirical formula will be found in the Formula Index, p. 2595.

FORMULA INDEX.

The following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides and cyanides of quaternary ammonium bases, however, are registered as group-substances.

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